Access DB# 129042

SEARCH REQUEST FORM

Scientific and Technical Information Center

Requester's Full Name: Wayne Langel Examiner #: 60603 Date: 8-4-04
Art Unit: 1754 Phone Number ~~30~~ 2-1353 Serial Number: 10/089689
Mail Box and Bldg/Room Location: E09A29 Remsen Results Format Preferred (circle): PAPER DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

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Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc, if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: Method for preparing phosphorus pentoxide powder with enhanced fluidity

Inventors (please provide full names): Vincent Magne

Earliest Priority Filing Date: 8-2-00

**For Sequence Searches Only* Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.*

Please search claims 1-6, as attached hereto.

(NOT MUCH REAL CLOSE)

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STAFF USE ONLY	Type of Search	Vendors and cost where applicable
Searcher: EJ	NA Sequence (#) ____	STN ____
Searcher Phone #: ____	AA Sequence (#) ____	Dialog ____
Searcher Location: ____	Structure (#) ____	Questel/Orbit ____
Date Searcher Picked Up: ____	Bibliographic ____	Dr.Link ____
Date Completed: 8-10-04	Litigation ____	Lexis/Nexis ____
Searcher Prep & Review Time: ____	Fulltext ____	Sequence Systems ____
Clerical Prep Time: ____	Patent Family ____	WWW/Internet ____
Online Time: ____	Other ____	Other (specify) ____

PTO-1590 (8-01)

CLAIMS

1. A process for the preparation of a phosphorus pentoxide (hexagonal variety) powder with improved flowability, characterized in that said phosphorus pentoxide powder is subjected to mechanical stirring by the dry route at ambient temperature under a dry gas atmosphere for a period of time ranging from 5 minutes to 30 minutes.

2. The process as claimed in claim 1, characterized in that the mechanical stirring time is between 10 and 20 minutes.

3. The process as claimed in either of claims 1 and 2, characterized in that the stirring rate of the device used for carrying out the process ranges from 100 rev/min to 350 rev/min.

4. The process as claimed in claim 3, characterized in that the stirring rate is between 150 rev/min and 300 rev/min.

5. The process as claimed in any one of claims 1 to 4, characterized in that it is carried out at a temperature ranging from 15 to 30°C.

6. A phosphorus pentoxide (hexagonal variety) powder obtained as claimed in one of claims 1 to 5, exhibiting a Hausner ratio Hr, defined as being the ratio of the tamped apparent density d_t to the aerated apparent density d_a, of equal to or less than 1.25.

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=> file reg
FILE 'REGISTRY' ENTERED AT 15:19:01 ON 10 AUG 2004
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
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=> display history full l1-


     FILE 'REGISTRY' ENTERED AT 14:04:51 ON 10 AUG 2004
                    E PHOSPHORUS PENTOXIDE/CN
L1                1 SEA "PHOSPHORUS PENTOXIDE"/CN

     FILE 'LCA' ENTERED AT 14:05:23 ON 10 AUG 2004
L2            32136 SEA (PRODUC? OR PROD# OR GENERAT? OR MANUF? OR MFR# OR
                    CREAT? OR FORM## OR FORMING# OR FORMAT? OR MAKE# OR
                    MADE# OR MAKING# OR FABRICAT? OR SYNTHESI? OR PREPAR? OR
                    PREP#)/BI,AB

     FILE 'HCA' ENTERED AT 14:06:37 ON 10 AUG 2004
L3             4538 SEA L1/P OR L2(2A)(L1 OR (PHOSPHORUS# OR P)(W)(PENTOXIDE#
                     OR PENTAOXIDE#) OR P2O5)
L4            68358 SEA L1 OR (PHOSPHORUS# OR DIPHOSPHORUS# OR P)(W)(PENTOXID
                    E# OR PENTAOXIDE#) OR P2O5
L5           789749 SEA FLOW OR FLOWS OR FLOWED OR FLOWING# OR FLOWABIL? OR
                    FLOWABL?
L6           195134 SEA STIR OR STIRS OR STIRRED OR STRIRRING# OR STIRABIL?
                    OR STIRABL?
L7            16902 SEA (MECH# OR MECHANICAL?)(2A)(MIX? OR BLEND? OR AGITAT?
                    OR ADMIX? OR COMMIX? OR IMMIX? OR INTERMIX?)
L8            36687 SEA (REV# OR REVOLUTION?)(2A)(M OR MIN# OR MINUTE?) OR
                    RPM OR R(W)P(W)M
L9               82 SEA HAUSNER#
L10               1 SEA L4 AND L9
L11            1482 SEA L4 AND L5
L12              58 SEA L11 AND L6
L13               9 SEA L12 AND L3
L14             129 SEA L3 AND L6
L15               9 SEA L14 AND L5
L16               1 SEA L14 AND L7
L17               4 SEA L14 AND L8
L18            2929 SEA L4 AND L6
L19              58 SEA L18 AND L5
L20               9 SEA L18 AND L7
L21              44 SEA L18 AND L8
L22             129 SEA L18 AND L3
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L23            75 SEA L4 AND L5 AND (L6 OR L7 OR L8)
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L25             4 SEA L19 AND L21
L26            58 SEA L19 AND L23
L27             4 SEA L21 AND L23
L28         11224 SEA APPARENT?(3A)(D OR DENS?)
L29           390 SEA AERAT?(3A)(D OR DENS?)
L30            69 SEA L4 AND L28
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                  OR L31 OR L33
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L39            15 SEA L23 NOT (L36 OR L37 OR L38)
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=> file hca
FILE 'HCA' ENTERED AT 15:19:16 ON 10 AUG 2004
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=> d l36 1-32 cbib abs hitind
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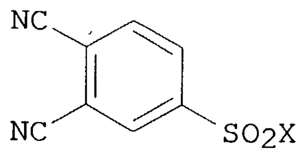
L36 ANSWER 1 OF 32 HCA COPYRIGHT 2004 ACS on STN

138:204840 Method for preparation of 4-halosulfonylphthalonitrile and their conversion into 4-phthalonitrile derivatives. Terao, Koichi (Seiko Epson Corp., Japan). Jpn. Kokai Tokkyo Koho JP 2003055335 A2 20030226, 16 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 2001-248227 20010817.

GI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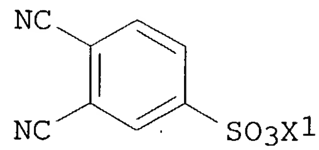
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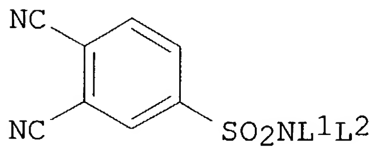
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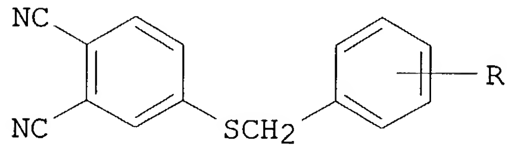
IV

AB 4-Halosulfonylphthalonitrile (I; X = halo) undergoes hydrolysis in the presence of an acid or alkali to give 4-sulfophthalonitrile (3,4-dicyanobenzenesulfonic acid), reaction with alkali hydroxide to give 3,4-dicyanobenzenesulfonic acid salts [II; X1 = (Q)1/n; wherein Q = alkali or alk. earth metal, quaternary ammonium; n = a valency of Q], and amidation with amines to give 3,4-dicyanobenzenesulfonamides (III; L1, L2 = H, C1-4 alkyl). The starting material I is prepd. by contacting 4-benzylthiophthalonitrile derivs. (IV; R = H, C1-4 alkyl) with halogen mols. such as Br, Cl, and I in aq. acid soln. or org. solvent contg. H2O for halogenation. These processes readily give in high yields the 4-phthalonitrile derivs. which are useful as intermediates for phthalocyanine compds. widely used for printer inks and optical recording materials. Thus, 25.0 g 4-benzylthiophthalonitrile was dissolved in a soln. of 210 mL AcOH and 40 mL H2O and cooled to 5-10°, followed by introducing 22.5 g Cl into the soln. at 5-10° over 1 h, and the resulting mixt. was **stirred** at the same temp. for 1 h, poured into ice-water, and **stirred** for .apprx.1 h to give, after filtering the pptd. crystals, successively washing them with H2O and isopropanol, and drying at 40° under the **flow** of air to give 16.6 g 4-chlorosulfonylphthalonitrile (V). V (4.1 g) was added portionwise to 40 mL 28% aq. NH3 at 5-10° under ice-cooling, **stirred** at room temp. overnight (8 h), adjusted to pH 1-2 adding dropwise concd. HCl to give, after filtering the pptd. crystals, washing them with distd. water, and drying at 50° under the **flow** of air to give 2.6 g 4-sulfonamidophthalonitrile (3,4-dicyanobenzenesulfonamide).

IC ICM C07C303-02
ICS C07C303-22; C07C303-38; C07C309-57; C07C311-16; C07B061-00

CC 25-20 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)
Section cross-reference(s): 26

IT 75-44-5, Phosgene 603-35-0, Triphenylphosphine, reactions

1314-56-3, Phosphorus pentoxide,
reactions 10025-87-3, Phosphorus oxychloride
(**prepn.** of bromophthalonitrile by dehydration of bromophthalamide with dehydrating agent)

L36 ANSWER 2 OF 32 HCA COPYRIGHT 2004 ACS on STN
136:169897 **Preparation** of **phosphorus pentoxide** powder with enhanced fluidity by mechanical treatment. Magne, Vincent (ATOFINA, Fr.). PCT Int. Appl. WO 2002012119 A1 20020214, 18 pp. DESIGNATED STATES: W: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (French). CODEN: PIXXD2. APPLICATION: WO 2001-FR2527 20010802. PRIORITY: FR 2000-10348 20000804.

AB **Phosphorus pentoxide** powder **produced** by air oxidn. of white phosphorus is treated mech. to enhance its fluidity. The **P2O5** powder is **mech. agitated** under a dry gas atm. at 15-30°C for 10-20 min at a rotation velocity of 150-300 **rpm**. The obtained hexagonal **P2O5** powder has a **Hausner** ratio of ≤ 1.25.

IC ICM C01B025-12

CC 49-2 (Industrial Inorganic Chemicals)

ST **phosphorus pentoxide** powder **mech agitation** fluidity enhancement

IT **Flow**
(enhancement of; **prepn.** of **phosphorus pentoxide** powder with enhanced fluidity by mech. treatment)

IT Powders
(**flow** enhancement of **P2O5**; **prepn.** of **phosphorus pentoxide** powder with enhanced fluidity by mech. treatment)

IT Air
(oxidant; **prepn.** of **phosphorus pentoxide** powder with enhanced fluidity by mech. treatment)

IT **Agitation (mechanical)**
(**prepn.** of **phosphorus pentoxide** powder with enhanced fluidity by mech. treatment)

IT **1314-56-3P, Phosphorus pentoxide, preparation**
(mech. treatment of; **prepn.** of **phosphorus**

pentoxide powder with enhanced fluidity by mech.
treatment)
IT 7723-14-0, Phosphorus, reactions
(white, oxidn. of; **prepn.** of **phosphorus**
pentoxide powder with enhanced fluidity by mech.
treatment)

L36 ANSWER 3 OF 32 HCA COPYRIGHT 2004 ACS on STN
132:333918 Manufacture of calcium superphosphate from defluorinated slag. Wu, Zhaoqiang; Zeng, Deren; Ai, Xincheng; Peng, Zhigao; Xu, Changshou (Phosphorous Calcium Fertilizer Plant, Weiyuan County, Peop. Rep. China). Faming Zhuanli Shenqing Gongkai Shuomingshu CN 1206701 A 19990203, 7 pp. (Chinese). CODEN: CNXXEV. APPLICATION: CN 1998-111987 19980427.
AB The raw material of the calcium superphosphate is composed of ground phosphorite (contain 34% of **P2O5**) 30-35%, defluorinated slag (contain 22-28% of **P2O5**) 30-35%, H2SO4 25%, and water 10-15%. The content of **P2O5** in the **produced** calcium superphosphate is 16-20%. The process comprises mixing, and allowing all ingredients to react at 105-125° for 20-30 min to obtain fresh calcium superphosphate, and curing to obtain fluffy product. The **flow** rates of H2SO4 and ore slurry, the temp. of the ore slurry, and the free acid (**P2O5**) content in the ore slurry are controlled to 1, 3.5 m3·h-1, 110-135°, and 15-18% resp. while mixing. The fresh calcium should be **stirred** every 8 h at 60-80° during May-August and every 24 h at 50-80° in other months resp. while curing.
IC ICM C05B011-08
CC 19-6 (Fertilizers, Soils, and Plant Nutrition)

L36 ANSWER 4 OF 32 HCA COPYRIGHT 2004 ACS on STN
128:16100 Isothermal oxidation of white phosphorus dispersed in water in a **stirred**-tank reactor. Mathews, Joseph B.; Jefcoat, Irvin A. (Olin Chem. Corp., Charleston, TN, USA). Journal of the Air & Waste Management Association, 47(10), 1103-1110 (English) 1997. CODEN: JAWAFC. Publisher: Air & Waste Management Association.
AB A global, first-order kinetic model fit data for the isothermal wet oxidn. of elemental white P (P4) in a batch, **stirred**-tank reactor. The initial white phosphorus solids concn. was held const. at 1 g/L while an air **flow** of 2.0 std. L/min supplied O for the reaction. A CD6-like turbine and an A2 impeller were evaluated at speeds from 1000-2250 **rpm**. For the CD6-like turbine, mass transfer effects were assumed to be eliminated above 2000 **rpm**; thus, the CD6-like turbine with a speed of 2250 **rpm** was selected for isothermal studies. Particle size and temp. were varied. For isothermal conditions, the first order

kinetic const. was 0.022/min at 46° to 0.078/min at 80°. The apparent activation energy was 6.78 kcal/mol. O reacted with suspended P4 particles forming oxides of P, primarily **phosphorus pentoxide** (P4O10 or **P2O5**). Some of the **P2O5** reacted with water to form PO43- as the primary product of white P oxidn. The amt. of **phosphorus pentoxide** absorbed in water increased with temp. The rate of PO43- formation followed zero order kinetics and was independent of particle size. As temp. increased, the PO4:PO3 ratio increased. This observation and the apparently low activation energy suggested that diffusion effects may not have been completely eliminated.

CC 60-2 (Waste Treatment and Disposal)
Section cross-reference(s): 49, 67

ST isothermal oxidn white phosphorus; **stirred** tank reactor oxidn white phosphorus; kinetics isothermal oxidn white phosphorus

IT Wastewater treatment
(oxidn., isothermal wet; particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred**-tank reactor)

IT Oxidation kinetics
(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred** -tank reactor)

IT Phosphates, processes
(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred** -tank reactor)

IT Solid wastes
(white phosphorus contg.; particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred**-tank reactor)

IT **1314-56-3, Phosphorus pentoxide,** processes
(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred** -tank reactor)

IT 12185-10-3, White phosphorus, processes
(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred** -tank reactor)

IT 7782-44-7, Oxygen, reactions
(particle size and temp. effect on isothermal wet oxidn. of white phosphorus dispersed in water and sludge in **stirred** -tank reactor)

L36 ANSWER 5 OF 32 HCA COPYRIGHT 2004 ACS on STN
120:326859 Removal of heavy metals especially cadmium, lead and mercury from extractive phosphoric acid. Teren, Jan; Hutar, Eduard; Gabco,

Milan (Czech Rep.). Czech. CS 275029 B2 19920115, 9 pp. (Czech). CODEN: CZXXA9. APPLICATION: CS 1989-1494 19890310.

AB Heavy metals ar removed from crude H3PO4 by pptn. in the form of sulfides at 15-95°. The reaction mixt. is **stirred** by circulation, pneumatic **mixing**, and/or **mech. mixing**, substances accelerating clarification are optionally added, and the pptd. sludge is sepd. by settling, filtration, centrifuging, and/or flotation. Before, during, and/or after adding a source of the sulfidic S, 4.2 + 10-4-4.6 + 10-1 mol NH3, KOH, and/or NaOH/mol H3PO4 is added. NH3 is added in the form of NH3(g), NH3(l), or NH4OH. The procedure is esp. suitable for H3PO4 used for fertilizer manuf. Thus, crude H3PO4 was treated with 5 g 13% Na2S soln./kg H3PO4 and 25 g 25% NH4OH/kg H3PO4. The Cd content decreased from 79.9 to 2.3 mg/kg **P2O5**, and Pb content decreased from 0.56 mg/kg **P2O5** to trace.

IC ICM C01B025-237

CC 49-2 (Industrial Inorganic Chemicals)
Section cross-reference(s): 19

L36 ANSWER 6 OF 32 HCA COPYRIGHT 2004 ACS on STN

115:236161 Phosphorosulfide-containing compounds and their use as lubricant additives. Andress, Harry John, Jr.; Ashjian, Henry (Mobil Oil Corp., USA). Eur. Pat. Appl. EP 445970 A2 19910911, 5 pp. DESIGNATED STATES: R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE. (English). CODEN: EPXXDW. APPLICATION: EP 1991-301665 19910228. PRIORITY: US 1990-488581 19900305.

AB Lubricating compns. comprise a major proportion of a lubricating oil or grease and a minor amt. of the reaction products of C2-32-olefins with free S, with or without added H2S, P2S5, and **P2O5**, **prepd.** by reacting the olefins and the S in the molar ratio 1:2 to 2:1 with approx. 0.1-1 mol P2S5 and P2O5, and, optionally, an aliph. amine and/or alkene oxide. The compns. are manufd. by reacting S, with or without added H2S, with a C2-32-olefin, P2S5, and P2O5, at 50-150° under autogenous pressure in the above mol. ratios. These compns. have improved antiwear properties. A mixt. of S 11, P2S5 0.5, isobutylene 10, and H2S 5 mols was heated in an autoclave at 120° for 12 h, and cooled to 25°, after which 1.2 mol propylene oxide was added. The reaction mixt. was **stirred** at 50° for 8 h, after which 0.4 mol Primene 81R was added and the mixt. **stirred** at 50° for 2 h. In a (described) test at 390°F, base lubricating oils contg. 1 wt.% of the additives gave scar diam. at 500, 1000, 1500, and 2000 **rpm** 0.4, 0.4, 0.5, and 0.6, vs. 1.0, 1.31, and 2.08 mm, and not available, resp., for base oil not contg. the additive.

IC ICM C10M159-12

CC 51-8 (Fossil Fuels, Derivatives, and Related Products)

IT 115-11-7D, Isobutylene, reaction products with hydrogen sulfide and

phosphorus pentoxide and pentasulfide and sulfur 1314-56-3D, **Phosphorus pentoxide**, reaction **products** with hydrogen sulfide and olefins and phosphorus pentasulfide and sulfur mixts. 1314-80-3D, Phosphorus pentasulfide, reaction products with hydrogen sulfide and olefins and phosphorus pentoxide and sulfur mixts. 7704-34-9D, Sulfur, reaction products with hydrogen sulfide and olefins and phosphorus pentoxide and pentasulfide and sulfur mixts. 7783-06-4D, Hydrogen sulfide, reaction products with olefins and phosphorus pentoxide and pentasulfide and sulfur mixts.
(lubricating oil additives contg., for decreased wear)

L36 ANSWER 7 OF 32 HCA COPYRIGHT 2004 ACS on STN
94:183357 Color proof films. Liu, Shuchen (American Hoechst Corp., USA). Eur. Pat. Appl. EP 19896 19801210, 26 pp. (German). CODEN: EPXXDW. APPLICATION: EP 1980-102931 19800527.

AB As material for color proofs of the type of (CA 63: 15770a), esp. with dark shades, of high sensitivity, good support-coating adhesion, and scratch-resistivity, 40-80 μ polyester supports are coated with a 0.1-10 μ o-quinone-sensitized dyed or pigmented layer which contains 10-60% of an anionic H_3PO_4 mono- or diester surfactant (CA 56: 3585i), having a d. of 1.0-1.4 (25°), a **flow** point of <30°, and an acidity of 55-120 mg KOH per g to reach pH 5.0-5.5. The surfactants are reaction **products** of **P2O5** with a condensate of a C6-150 compd., such as a phenol, contg. ≥1 mol of a C2-4 alkylene oxide. The foils are UV-exposed through a pos. screened Ag color sepn. image, developed with an alk. soln., and then given an overall exposure to remove the yellow tint due to residual sensitizer. In neg.-working coatings the surfactants shorten the developing time. Thus, a Me methacrylate-methacrylic acid 85:15 copolymer 5.1 g was dissolved in MeOCH2CH2OH, **stirred** for 1 h with Orasol Yellow 3 GLG 0.86, Orasol Black 6.02, 2,3,4-trihydroxybenzophenone naphthoquinone-(1,2)-diazide-(2)-5-sulfonate 12.04, and GAF Gafac RE-610 surfactant 6.00 g, then filtered for coating a 76 μ biaxially oriented polyester support. Exposure through a pos. color sepn. and a step wedge for 20 s and development with aq. 9% Na lauryl sulfate, followed by a 20 s after-exposure, resulted in a pos. black sepn. image revealing 2 steps. Without the surfactant an exposure of 320 s was required to produce the same result.

IC G03F003-10; G03F007-08

CC 74-2 (Radiation Chemistry, Photochemistry, and Photographic Processes)

L36 ANSWER 8 OF 32 HCA COPYRIGHT 2004 ACS on STN
87:72431 Suspension for manufacturing foundry molds. Ivanov, V. N.; Chulkova, A. D. (Moscow Automobile Plant, USSR). Belg. BE 840650 19761012, 25 pp. (French). CODEN: BEXXAL. APPLICATION: BE

1976-166073 19760412.
AB Foundry molds with good mold-release properties, strength, dimensional stability, and life were prepd. from suspensions contg. an alkyl silicate binder 2.5-9, water 16.5-23, HCl 0.05-0.25, phosphoric acid deriv. 0.2-1.0, surfactant with plasticizing action 0.02-0.1%, and the balance refractory filler (av. particle size <50μ). Thus, a suspension of HCl (d. 1.15 g/cm3) 355, Cr Al phosphate (**P2O5**/(Al2O3 + Cr2O3) ratio 2.3) 415 cm3, Et silicate 40 (d. 1.05 g/cm3) 3.2 L, disodium sulfosuccinate [14933-03-0] 100 g, and powd. quartz 44 kg in 14.9 L water was **stirred** at 2800 **rpm** for 60 min. The viscosity of a 100 cm3 sample of the suspension **flowing** through a 4 min diam. orifice was 45 s which increased to 50 s after 48 h storage. A layer of the suspension was dried for 3 h and had flexure strength 57 and 107 kg/cm2 at 20 and 900°, resp. After 48 h storage at 17°, the values were 52 and 103.5 kg/cm2, resp.
IC B22C
CC 57-5 (Ceramics)
Section cross-reference(s): 55

L36 ANSWER 9 OF 32 HCA COPYRIGHT 2004 ACS on STN
87:25464 Trisodium monophosphate dodecahydrate with cubelike or beadlike crystal form. Liedloff, Bernd; Gisbier, Doris (Ger. Dem. Rep.). Ger. (East) DD 121502 19760805, 7 pp. (German). CODEN: GEXXA8. APPLICATION: DD 1975-188206 19750905.
AB Aq. H3PO4 is reacted at 70-80° with aq. NaOH to give a soln. having Na/P atom ratio of 3.1-3.3, sp. gr. 1.31-1.34, and **P2O5** 11-13%. The soln. is then **stirred** (Froude no. 0.026-0.062) and cooled during 16-23 to 30-40°. The product is free-**flowing**. It effloresces more slowly in air at 25-45° and also cakes less during storage than Na3PO4.12H2O needle crystals. Thus, 3.9 m3 of H3PO4 having sp. gr. 1.61 and 8.8 m3 of aq. NaOH having sp. gr. 1.50 were added simultaneously to 25 m3 of spent liquor (5% **P2O5**) contained in a crystallizer of 38 m3 capacity. The reaction temp. was 70-80° and the final reaction soln. had Na/P ratio of 3.18, sp. gr. 1.328 and contained 12.5% **P2O5**. It was cooled to 35.5° over 20 h while stirring at 30 **rpm** with a 1.6-m-diam. stirrer (Froude no. 0.04) to give a solids yield of 85.5% of the Na3PO4.12H2O which was in soln. The **product** contained **P2O5** 18.6, Cl 0.01, and insols. 0.02%. The sieve anal. was 1 mm, 2.1; 0.2-0.5 mm, 91.2; and <0.2 mm 6.7%.
IC C01B025-18
CC 49-5 (Industrial Inorganic Chemicals)

L36 ANSWER 10 OF 32 HCA COPYRIGHT 2004 ACS on STN
86:70779 Density, viscosity, and surface tension of nitroammophos and nitroammophoska melts. Nikandrova, Ya. T.; Artyushina, A. I.;

Avdyakova, O. S.; Nikandrov, I. S. (USSR). Tezisy Dokl. Vses. Nauchno-Tekh. Konf. Tekhnol. Neorg. Veshchestv Miner. Udobr., 9th, Volume 1, 58. Editor(s): Amirova, S. A. Permsk. Politekh. Inst.: Perm, USSR. (Russian) 1974. CODEN: 34PSAU.

AB The H2O content (0-5.5%) had no effect on the d. of the melt at 140-185°. When KCl was added the **apparent d.** decreased (at 180°) by a factor of 1.1 and when KNO3 or K phosphate (10% K2O) was added the **apparent d.** increased by 30-40 kg/m3. Equations describing the temp. relations of the nitroammophos and nitroammophoska melt d. and viscosity are presented. The energy of activation of the viscous **flow** decreased with H2O content increasing (0.5-5.5%). When the H2O content increased to 10% the activation energy increased to 8.5 kcal/mole; the melt viscosity increased 1.2-1.3-fold when even 2.4% K2O was added. A linear relation between surface tension of the melts and temp. and a decrease in the surface tension with increasing K2O content of the melt were obsd. At 170° and H2O content 2%, the d. of nitroammophos having a N/**P2O5** ratio 1:1 was 1508 kg/m3; its viscosity and surface tension were 0.0107 nsec/m2 and 0.1037 nsec/m, resp.

CC 19-5 (Fertilizers, Soils, and Plant Nutrition)
Section cross-reference(s): 49

L36 ANSWER 11 OF 32 HCA COPYRIGHT 2004 ACS on STN

76:49612 Treating digestion tank water to remove phosphorus compounds. Dunseth, Maria G.; Brinkman, Joel J. (W. R. Grace and Co.). Ger. Offen. DE 2123669 19711125, 16 pp. (German). CODEN: GWXXBX. PRIORITY: US 19700513.

AB At least 80% by wt. total P is removed from digestion tank water when kept 30-120 min at 60-75° at atm. pressure or at at least 55°/710 mm or at lesser temp. and pressure and the solid matter is sepd. from the water. In treatment of water in which the proportion of hard ions is stoichiometrically less than that required theoretically for pptn. of the contained phosphates as orthophosphate salts, the addn. of MgO is suggested. Thus, a 2-l. sample of sewage contg. 120, 100, 80, 70, and 330 mg/l. Ca, Mg, total P, orthophosphate, and total N heated at 65° and **stirred** 2 hr at 100 **rpm** with increase of pH from 7.0 to 8.8, centrifuged and analyzed showed elimination of 95% total P and 77% total N. The BOD and COD diminished from 297 to 130 mg/l. and from 560 to 364 mg/l., resp. The residual solids contained 19.5% **P2O5** in a **form** suitable for use by plants.

IC C02C

CC 60 (Sewage and Wastes)
Section cross-reference(s): 61

L36 ANSWER 12 OF 32 HCA COPYRIGHT 2004 ACS on STN

74:41489 Continuous preparation of an aqueous ammoniated phosphate

composition. Mullen, George C., Jr. (Standard Oil Co.). U.S. US 3459499 19690805, 8 pp. (English). CODEN: USXXAM. APPLICATION: US 1966-546411 19660429.

AB In production of ammonium polyphosphate soln. by reacting NH3 and wet-process superphosphoric acid (which contains polyphosphates), it is important to avoid hydrolysis of the polyphosphate because otherwise the metal compds. sequestered by the polyphosphate will ppt. In the process claimed, the NH3 and superphosphoric acid are introduced at points remote from each other into a large body of **stirred** ammonium polphosphate soln. In an example, NH3 and H2O in the required amts. were introduced into a stream of recycled soln. and the mixt. **flowed** into the reactor where wet-process superphosphoric acid (72% **P2O5**) was sparged in. Good quality product soln. (10% N, 33.5% **P2O5**) was **produced**; <1% of the polyphosphate was hydrolyzed.

IC C01B; C05B

NCL 023107000

CC 20 (Fertilizers, Soils, and Plant Nutrition)

L36 ANSWER 13 OF 32 HCA COPYRIGHT 2004 ACS on STN

73:47141 Low density ammonium polyphosphates. (Knapsack A.-G.). Fr. Demande FR 2009787 19700206, 6 pp. (French). CODEN: FRXXBL. PRIORITY: DE 19680531.

AB Long chain NH4+ polyphosphates having the general formula (NH4)n+2PnO3n+1 are prepd. by treating polyphosphoric acid with NH3 at 310-30°. Thus, 5.035 kg polyphosphoric acid (84% **P2O5**) at 90° is treated with 1.5 std. m3 NH3/hr, and the mixt. is held at 310-20°. After 30 min, when neutralization is complete, NH3 **flow** is reduced to 0.4 m3/hr, and the mixt. is held at 245° to sep. a melt in less than an hr. The mixt. is cooled, washed with H2O (to ext. short chain polyphosphates), and dried under vacuum at 70° to recover 5.28 kg of cryst. product (I) contg. 72.8% **P2O5** and having an **apparent d.** 0.39 kg/l. with n = 110. Also, n = 350 when 50 kg I (at 30 kg/hr) is heated for 50 min at 310° in an NH3 atm.

IC C01B

CC 49 (Industrial Inorganic Chemicals)

L36 ANSWER 14 OF 32 HCA COPYRIGHT 2004 ACS on STN

71:128426 Purification of recirculating waters of the "Fosforit" Kingisepp plant concentrating mill. Shifrin, S. M.; Varyukha, D. N. (USSR). Sanit. Tekh., 7-12. Editor(s): Shifrin, S. M. Leningrad. Ordena Trudovogo Krasnogo Znameni Inzh.-Stroit. Inst.: Leningrad, USSR. (Russian) 1967. CODEN: 21IRAS.

AB Water which has been used in the process of beneficiation of phosphate ore, contained up to 85,000 mg./l. of suspended solids and materials used in flotation both org. and inorg. Purification was

carried out by (a) sedimentation, (b) coagulation with polyacrylamide 0.1 mg./l. as coagulant, (c) biocoagulation by using activated sludge 0.1 ml./l. and **aeration** for 70 min., (**d**) biol. purification with the activated sludge process. Sedimentation decreased the amt. of suspended solids to 477.2 mg./l. in 30 min. and to 229.3 mg./l. in 60 min. Further increase in the time of sedimentation did not give any significant improvement. Coagulation (b) gave an effluent contg. 60 mg./l. of suspended solids after 30 min. of sedimentation. Biocoagulation removed 65% of suspended solids. In biol. purification, NH4Cl 20 mg./l. and Na phosphate 10 mg./l. of **P2O5** were added and treatment was carried out on a lab. scale in cylindrical tanks of 56-1. capacity. The whole was aerated from 12 to 25 hrs. The treatment lowered B.O.D. from .apprx.300 to 11 mg./l.

CC 60 (Sewage and Wastes)

L36 ANSWER 15 OF 32 HCA COPYRIGHT 2004 ACS on STN

71:12458 Synthesis and selection of catalysts for the oxidation of propylene to acrolein. Lemberanskii, R. A.; Aliev, V. S.; Kyazimov, Sh. K.; Efendiev, R. M. (USSR). Azarbaycan Neft Tasarrufati, 48(1), 34-6 (Russian) 1969. CODEN: AZNKAY. ISSN: 0365-8554.

AB The oxidn. of C3H6 to acrolein was studied in a lab. **flow**-through glass reactor under the following conditions: duration of the expts. 30-1500 hrs., temp. 425-500°, contact time 1.74-2.35 sec., and the content of C3H6 in the gas-air mixt. 1.87-25.0 vol. %. The catalysts investigated contained Bi2O3 (10.29-62.8 wt. %), MoO3 (3.21-37.2 wt. %), and **P2O5** (0.0-0.5 wt. %) supported on silica gel, α-Al2O3, and corundum. Following compds. were found in the reaction products: acrolein 45.0-84.0, HCHO 0.227-6.66, MeCHO 0.45-13.22, MeCO2H 0.56-12.5, CO2 3.70-32.4, CO 0.0-7.6, and H2O 3.4-10.2 wt. %. The conversion was 10.7-52.0 wt. % based on C3H6. Best results (conversion 34-5 wt. %, selectivity for acrolein 72-4 wt. %) were obtained at 500°, contact time 2 sec., and 25.0 vol. % C3H6 in the gas-air mixt. on the catalyst contg. Bi2O3 11.5, MoO3 8.02, and **P2O5** 0.5 wt. % supported on corundum (bulk d. 2.055 g./cm.3, **apparent d.** 3.09 g./cm.3, porosity 21%, and the sp. surface area 0.6-1.2 m.2/g.).

CC 23 (Aliphatic Compounds)

IT 1304-76-3 1313-27-5, uses and miscellaneous **1314-56-3**
(catalysts, for oxidn. of propene)

L36 ANSWER 16 OF 32 HCA COPYRIGHT 2004 ACS on STN

66:117466 Productive use of phosphate slurry. (Knapsack A.-G.). Neth. Appl. NL 6608852 19670116, 10 pp. (Dutch). CODEN: NAXXAN. PRIORITY: DE 19650714.

AB The slurry obtained by neutralization of wet process H3PO4 with alkali to pH 4-10 can be used economically when mixed with finely

ground phosphate ore and made into shaped pieces for electrolytic production of P, provided the mixt. contains <15% slurry by wt. on dry basis. The slurry consists of phosphates of Fe, Al, Ca, and Mg, with .apprx.60% of H2O both occluded and as H2O of crystn. The dry material contains .apprx.50% **P2O5**. The slurry is **stirred** with H2O, or with the usual binders or fillers, e.g. clay, phosphate powder, or finely divided phosphate and alkali phosphates, so as to give a mixt. contg. 25-40% solids by wt., and this is then mixed with the phosphate ore, which is pressed into shapes or granulated, dried at 300-400°, and sintered. In this way the **P2O5** in the slurry, may be obtained as P, the pressure- and abrasion-resistance of the granules or other solid forms are increased, and the use of binders may be avoided or decreased. In an example, 10 kg. phosphate slurry assocd. with 60% H2O by wt., was suspended in 60 kg. H2O in a mixing vessel to give a comparatively easy **flowing** mixt. contg. 25% dry material; 350 kg. of ground phosphate ore was granulated with 100 kg. of this mixt. in a rotary granulator. The moist granules contained 16.5% H2O by wt. and .apprx.8.9% dried slurry on the basis of the phosphate ore. After drying and sintering at .apprx.950° the granules had a pressure resistance at the center of 75-80 kg. and an abrasion resistance of 85-90% detd. by rolling 1000 kg. of sintered pellets for 30 min. in a 300 mm. diam. cylinder at 80 **rpm**. and finding the amt. with size <0.5 mm.

IC C01B

CC 49 (Industrial Inorganic Chemicals)

L36 ANSWER 17 OF 32 HCA COPYRIGHT 2004 ACS on STN

66:96941 Concentration of aqueous solutions and suspensions. (SINCAT Societa Industriale Catanese S.p.A.). Neth. Appl. NL 6608226 19661219, 18pp. (Dutch). CODEN: NAXXAN. PRIORITY: IT 19650618.

AB The soln. or suspension to be concd. is dispersed in a rapid stream of hot gases rising in a container with increasing cross section. The rate of **flow** of the gas thus gradually diminishes until conditions become favorable for the formation of a fluidized bed of drops with practically stable dimensions, in which the drops come into very efficient direct contact with the gas, and are rapidly concd. at a comparatively low temp. As they lose H2O, the drops become smaller and their **apparent d.** sometimes decreases, and they are then carried along by the gas. They are cooled and may easily be sepd. at the outlet, e.g., by a cyclone separator. In the app. described, gases at 70-1100° pass into the lower section of a practically vertical elongated vessel having a constriction above the gas inlet, in which the gases reach a velocity of 50-70 m./sec., followed by a section with an upward increase in diam. having the form of a truncated cone with included angle 6-9°. A section with const. diam. follows, joined by a tube with decreasing diam., in which the gases are again

accelerated, to a bend leading to the separator. The soln. or suspension is introduced at the constriction. The occurrence of incrustations on the walls and of blockages is largely avoided. Thermal equil. is rapidly established, and the gas remains in contact with the liquid during the concg. stage for only some tenths of a sec. Good results are obtained with solns. of H3PO4, H2SO4, hydroxides, Na2CO3, NaHCO3, (NH4)2SO4, NH4NO3, NH4H2PO4, KNO3, KCl, K2SO4, Ca(NO3)2, MgSO4, MgCl2, and fertilizer suspensions from which a granulated product may be manufd. From substances with a low m.p. a molten product may be obtained at the outlet. In H3PO4 concn. the formation of mist is avoided, and starting with 30% **P2O5** by wt. a product with 64% **P2O5** may be obtained. Operating conditions can be changed rapidly, and when it suddenly becomes necessary to store the product, production of highly concd. acid gives best use of available storage facilities. In concg. 30% H3PO4 contg. 2% F to 50% **P2O5** by wt., 70-5% of the F is removed, and 90% when concg. to 64%. The F compds. are comparatively easy to recover from the residual gases. Because of rapid concn., app. with small dimensions can give high production. The gases used in the process can be air heated in a combustion chamber, or various waste gases from other processes which would be normally discharged to the atm., provided they have a low moisture content, a suitable temp., and do not react with the substances to be concd. In an example, a concentrator was used consisting of a vertical Venturi tube with a 500 mm. long narrow portion with internal diam. 214 mm. The included angle of the diffusor was 7°. Above the Venturi tube was a tube with a const. diam. of 500 mm. The product was sepd. in a cyclone and collected at its exit. Approx. 2210 standard m.3 of air/hr. at 650° was used with a velocity of .apprx.49 m./sec. in the constriction, and .apprx.5 m./sec. at the exit from the diffusor. A soln. (1365 kg./hr.) at 65° contg. 43% (NH4)2SO4 and 57% H2O was fed in at the constriction and .apprx.965 kg./hr. of a suspension contg. 25.4% crystd. (NH4)2SO4, 35.9% (NH4)2SO4 soln., and 38.7% H2O was obtained.

IC B01D

CC 48 (Unit Operations and Processes)

L36 ANSWER 18 OF 32 HCA COPYRIGHT 2004 ACS on STN

66:30583 Preparation of phosphoric acid. (Societe PROREA). Neth. Appl. NL 6600968 19660803, 24 pp. (Dutch). CODEN: NAXXAN. PRIORITY: FR 19650203 - 19650903 19650903.

AB Improved filtration during wet process manuf. of H3PO4 is obtained by dispersing broad, flat, very thin streams of H2SO4 into a well-**stirred** circulating phosphate slurry. Addn. of natural phosphate can immediately precede or follow addn. of H2SO4, depending on its reactivity and fineness. Conditions can be regulated so that H3PO4 and CaSO4.xH2O are formed, with x = 2, 1/2, or 0. Preferably x = 2, and the formation of gypsum crystals is

favored by the immediate and practically complete dispersion of the H2SO4, which avoids pptn. of anhydrite and α-semihydrate, and the formation of too many seed crystals of gypsum, allowing the crystals already present to grow more regulary. If the temp. of the slurry is brought to .apprx.70° immediately after dispersion of the H2SO4, crystals with dimensions 200-300 μ are formed. When this temp. is brought initially above 70°, a microscopic ppt., probably of unstable β-semihydrate, is formed, and if the temp. is then suddenly reduced to 70° at the outflow from the dispersion vessel, this avoids formation of α-semihydrate, which would take 10-36 hrs. to be transformed to gypsum, and the gypsum crystals already present then grow at the expense of the ppt. to attain dimensions 800-1000 μ. The cooling can be achieved by rapid mixing of the circulating slurry with wash water from the sepn. of the H3PO4 and gypsum, or with slurry cooled to 70° by blowing in air or by vacuum evapn. When, simultaneously with the addn. of natural phosphate, H2SO4 and wash water are dispersed close together in the same vessel, the temp. may be controlled so that gypsum crystals form with dimensions .apprx.600μ. Finally an amt. of slurry is withdrawn from circulation corresponding to the production of H3PO4 and gypsum, and these are sepd., e.g. by filtration or centrifugation. A plant for the process is described consisting of a series of vessels through which the circulating slurry **flows**, and in the 1st of which the initial reactions take place, to be concluded in the following vessels in which ripening of the slurry takes place, part of which is withdrawn for sepn. of H3PO4 and the crystals formed. Connecting lines are provided between the ripening and reaction vessels, and with a circuit through a vacuum evaporator, to enable electronic control of the regulating valves to bring the temp. to the desired value. The vessel in which the initial reactions take place consists of divisions, in the 1st of which phosphate is added to the slurry, and in the 2nd of which the H2SO4 is dispersed. A single vessel may be used for the addn. of phosphate and the simultaneous dispersion of H2SO4 and wash water. A special dispersion app. is described having openings or small channels next to one another so as to disperse H2SO4 and wash water mixed completely at the moment at which they come into contact with the slurry. This dispersal unit also **stirs** the medium, and has a hollow axle and blades with sep. channels for H2SO4 and wash water, which come together at the ends of the blades and are simultaneously dispersed. Scoops, the height of which is adjustable, may be fitted above the dispersal zone for thorough stirring. In the plant described 9.5 kg./hr. of Moroccan phosphate with 34% **P2O5** and 8.9 kg./hr. 98% H2SO4 were added. The primary slurry circulated at 190 kg./hr. The temp. at the outlet from the H2SO4 disperser was 88°, and the crystn. temp. in the 2nd and 3rd vessels was 70-2°, and 69-70° in the 4th. H3PO4 was **produced** with 32% **P2O5**

and 2.5% H_2SO_4. Easily filterable diamond-shaped crystals with dimensions 800-1000 μ were formed. The total yield of **P_2O_5** was 98.5%.

IC C01B

CC 49 (Industrial Inorganic Chemicals)

L36 ANSWER 19 OF 32 HCA COPYRIGHT 2004 ACS on STN

64:57922 Original Reference No. 64:10795d-g Wet-process phosphoric acid and utilization of the by-product gypsum. Roy, A. K.; Bardhan, M. K.; Singh, R. U. (Fertilizer Corp. India, Ltd., Sindri). Technology (Sindri, India), 2(2), 71-5- (English) 1965. CODEN: TCNOAQ. ISSN: 0040-1641.

AB The prepn. of phosphoric acid from Makatea and Morocco varieties of rock phosphate was studied. The suitability of the by-product gypsum obtained was compared with 2 com. samples of by-product gypsum for the production of $(NH_4)_2$-SO_4. In the usual process, rock phosphate is treated with H_2SO_4 in the presence of recycle phosphoric acid; gypsum is a by-product. Since the quantity of gypsum is about 4.5 tons per ton of **P_2O_5 produced**, its disposal is a major problem in the industry. The Merseburg process involves the reaction of gypsum with $(NH_4)_2CO_3$ to make $(NH_4)_2SO_4$. In the absence of indigenous sources of S in India, the production of $(NH_4)_2SO_4$ from by-product gypsum is attractive because the sulfate radical is used twice. Thus, 75 g. rock phosphate (80% through 100 mesh B.S.) was placed in a 3-neck **stirred** 3-l. flask, maintained at 70 ± 5°. Phosphoric soln. of measured concn. and vol. was then added and the mixt. was **stirred** for 4-5 min. at 90 **rpm**. Dil. H_2SO_4 was then added slowly with a slight increase in the stirrer speed. During the reaction, a slight vacuum, 12 mm. of H_2O, was maintained on the reaction flask. After the reaction, the slurry was filtered under a vacuum of 20 in. Hg through a No. 1 Whatman filter paper and the filtration time noted. Filter cakes were washed with dil. phosphoric acid and finally with distd. H_2O. The washed cakes were dried at 45° and analyzed. A reaction time of 4 hrs. was found to give the best filterability and min. residual F and P_2O_5 in the gypsum. The conversion efficiency with Morocco phosphate was slightly better than with the Makatea variety. Gypsum from the former also had better filterability. The filterability of the magma is the most important factor in detg. the suitability of a particular gypsum for reaction with $(NH_4)_2CO_3$ soln. By this criteria, the 2 by-product gypsum samples from the Morocco and Makatea varieties of rock phosphate appear to be better suited for conversion to $(NH_4)_2SO_4$ than the 2 com. samples, but not as well suited as a sample of natural gypsum from Pakistan.

CC 17 (Industrial Inorganic Chemicals)

L36 ANSWER 20 OF 32 HCA COPYRIGHT 2004 ACS on STN

64:27167 Original Reference No. 64:4963h,4964a-h,4965a-g
Polyfluorobicyclo[2.2.1]heptanes. I. 1H-Undecafluoro- and 1H,4H-decafluorobicyclo[2.2.1]heptane and a novel elimination process. Campbell, S. F.; Stephens, R.; Tatlow, J. C. (Univ. Birmingham, UK). Tetrahedron, 21(11), 2997-3008 (English) 1965. CODEN: TETRAB. ISSN: 0040-4020.

GI For diagram(s), see printed CA Issue.

AB cf. CA 62, 16076f. Bicyclo[2.2.1]heptadiene (200 g.) passed over 6 kg. CoF3 at 250-300° in 3 hrs. and the product removed in a stream of N at 30 l./hr. in 1.5 hrs., trapped at -78° and the H2O-washed **product** dried over **P2O5**, the **product** (2.3 kg. from 5 runs) distd. through a vacuum-jacketed column packed with Dixon gauze rings and the fractionation controlled by gas chromatography over 1:2 dinonyl phthalate-kieselguhr (unit A) (100°, N **flow**-rate 1.0 l./hr.) gave fractions 1, b. 27-66° (130 g., 6 components); 2, b. 66-73° (172.3 g., 2 components): 3, b. 73-4.9° (210 g., 2 components); 4, b. 74.9-5.1° (99 g.); 5, b. 75.1-83.0° (162 g., 5 components); 6, 83-6.8° (116 g., 3 components); 7, b. 86.8-91° (161.6 g., 4 components); 8, b. 91-5° (206 g., 3 components); 9, b. 95-109.5° (146.8 g., 5 components); 10, b. 109.5-12° (148.9 g., 2 components); 11, b. 112° (284.3 g.); and 217 g. unidentified residue. Fraction 2 (8 g.) sepd. on unit A (70°, N **flow**-rate 14 l./hr.) gave 4 g. perfluoromethylcyclohexane and 2.5 g. perfluorobicyclo[2.2.1]heptane (I), m. 105-7° (sealed tube). Similar sepn. of fraction 3 (6 g.) gave 4.5 g. impure perfluoromethylcyclohexane and 0.7 g. I. Sepn. of 160 g. fraction 7 on a 1:2 dinonyl phthalate-kieselguhr Cu column (488 + 7.5 cm., unit C) at 92° with 40 l./hr. N **flow**-rate gave 60 g. 1H-undecafluorobicyclo[2.2.1]heptane (II), m. 94-6° (sealed tube). Fraction 8 (200 g.) taken up in C6H6 and sepd. on unit C at 82°, N-**flow**-rate 44 l./hr. yielded 130 g. II. Similar sepn. of fraction 10 (140 g.) in Et2O yielded 95 g. 1H,4H-decafluorobicyclo[2.2.1]heptane (III), m. 92-3° (sealed tube), b. 112°. Fraction 11 distd. from **P2O5** gave 280 g. III with correct ir spectrum. The substantial yield reflected the high chem. stability associated with a bridgehead hydrogen. II (2 g.) slowly sublimed in a stream of N (3.5 l./hr.) passing over **stirred** CoF3 at 250°, the product collected at -180° and sepd. on unit A at 90° in N at 17 l./hr. gave 0.6 g. I and 0.2 g. II. Similar fluorination of 2.0 g. III gave 0.3 g. I and 0.4 g. II. Similar fluorination of 2.0 g. III gave 0.3 g. I and 0.4 g. II. Both II and III were recovered unchanged after treatment with strong aq. KOH at 100° but underwent extensive deuteration when treated with KOH in D2O. II (2 g.), 10 g. KOH, and 10 g. D2O shaken 3 hrs. at 100° in a sealed Pyrex glass tube and the lower layer distd.

in vacuo gave 1.8 g. 80% deuterated material m/e 276, 275, 176, 175, 226, 225, reconverted to II on shaking 3 hrs. at 100° with KOH and H2O. Similar deuteration of 3 g. III gave 2.7 g. 70% deuterated material, m/e 259, 258, 257, 209, 208, 207, 178, 177, 176, 159, 158, 157, indicating the presence of .apprx.57% 1D,4D-decafluorobicyclo[2.2.1]heptane, 38% 1H,4D-decafluorobicyclo[2.2.1]heptane, and 5% III. The exchanges showed the transient formation of the carbanion (IV) under the purely inductive influence of 3 > CF2 groups in a satd. system without resonance stabilization of the anion by neighboring unsatd. groups. The general validity of the method of deuteration was indicated by comparable exchanges with C6HF5 (70%), 1H-nonafluorocyclohexene (65%), and F3CCHBrCl (95%). II (6 g.) in 80 ml. Et2O **stirred** at -40° with dropwise addn. of 0.98N MeLi in Et2O and evolution of 420 ml. CH4, the mixt. **stirred** at -40° 30 min. and treated with 20 ml. redistd. AcH, the mixt. **stirred** 30 min. at -40° and 1 hr. at 20°, dild. with 25 ml. 4N HCl and the washed and dried Et2O evapd., the residue (10.5 g.) analyzed over 1:2 silicone-gum-kieselgühr (unit B) and sepd. on a Cu column contg. 1:2 silicone-gum-kieselguhr gave 3.0 g. undecafluorobicyclo[2.2.1]heptylmethylcarbinol (V), m. 99-100°. V (0.5 g.) and a trace of hydroquinol distd. from **P2O5** gave 0.3 g. undecafluorobicyclo[2.2.1]heptylethylene, m. 49-50°. Other successful trapping expts. demonstrated the existence of the anion IV. With D2O at -55° the mixt. from treatment of II with MeLi in Et2O at -40° yielded 60% 1-deuterioundecafluorabicyclo[2.2.1]heptane, characterized by ir and N.M.R. spectroscopy. Br and MeBr at -55° similarly yielded 68% 1-bromoundecafluorobicyclo[2.2.1]heptane, m. 109-10°, and 1-methylundecafluorobicyclo[2.2.1]heptane, m. 125.5-6.5°. It was of considerable interest to exam. the thermal stability of IV. II (6 g.) in 400 ml. Et2O at -55° **stirred** with dropwise addn. of 1.1N MeLi (prepd. from MeI) in Et2O and the mixt. **stirred** 30 min. at -55°, kept 30 min. at 25-30° and refluxed gently 1 hr., filtered from pptd. LiF and the residue on evapn. sepd. by gas chromatography on a 1:2 silicone-gum-kieselguhr column gave a mixt. (2.4 g.) of Et2O and 2 minor components, sepd. on unit A to give small amts. of the olefin, 1H-nonafluorobicyclo[2.2.1]hept-2-ene (VI), and 4.8 g. 1-iodononafluorobicyclo[2.2.1]hept-2-ene (VII), b. 124-5°. VI (0.5 g.) and KMnO4 in Me2CO gave HO2CCF2CF2CO2H, isolated as its dianilinium salt (0.25 g.), m. 210-11°. VII (1 g.) passed over CoF3 at 280° in a stream of N and the product (0.9 g.) washed with H2O and distd. in vacuo over **P2O5** gave 0.5 g. I, showing retention of the norbornane skeleton. VI (0.9 g.) fluorinated over CoF3 at 140° gave 0.6 g. II. VII (3 g.) in 15 ml. Et2O **stirred** with 10 g. Mg in 90 ml. Et2O contg. a small crystal of iodine and the mixt. refluxed 2 hrs., treated

slowly with 30 ml. 3N H2SO4 and the isolated product (5.2 g.) sepd. on unit A gave 1.4 g. VI, m. 36-7°. An estn. of the stability of an ethereal soln. of the Li salt of IV was made by dividing the soln. at -55° into 3 parts of which the 1st was treated with AcH at -40° to give a 40% yield of V. The 2nd portion was kept 30 min. at 15° and then treated with AcH, giving 10% V and 18% VII. The 3rd portion was refluxed 1 hr. before addn. of AcH and gave 40% yield of VII only. The decompn. at 15° is much slower than that associated with non-bridgehead carbanions. II (1 g.) treated with MeLi (from MeBr) in 30 ml. Et2O at -55° and the system **stirred** 1 hr. at 20° with addn. of 10 g. D2O, the filtered dried Et2O layer evapd. in vacuo and the residue (3.3 g.) sepd. by gas chromatography on unit A gave 0.6 g. 1D-undecafluorobicyclo[2.2.1]heptane, ir spectrum differing in the range 3000-650 cm.-1 from that of II. The decompn. of Li salt of IV to VII presumably involves initial loss of F ion in a non-coplanar β-elimination to give a transient bridgehead olefin (VIII) or diradical of very short duration. Addn. of LiI (known to be present in ethereal MeLi prepd. from MeI) and loss of F ion from the adduct in a very facile cis-coplanar elimination gives VII. II (6 g.) in 400 ml. Et2O at -55° **stirred** with addn. of 1.03N MeLi (from MeBr) in Et2O and the isolated residue (6.3 g.) sepd. (3.5 g.) on a preparative scale gave 0.5 g. 9:1 mixt. of 1-methyl-undecafluorobicyclo[2.2.1]heptane (IX) and suspected 1-methyl-nonafluorobicyclo[2.2.1]hept-2-ene, together with 1.3 g. 1-bromononafluorobicyclo[2.2.1]hept-2-ene (X), b. 100°, contg. a small amt. of 1-bromoundecafluorobicyclo[2.2.1]heptane (XI). X (1 g.) in 5 ml. Et2O added dropwise with stirring to 0.3 g. Mg in 30 ml. gently refluxing Et2O and the mixt. refluxed 1.75 hrs., **stirred** with 25 ml. 4N H2SO4 and the washed, dried, and filtered Et2O layer evapd. in vacuo gave 1.9 g. residue sepd. by gas chromatography over unit A column at 65° to give 0.5 g. VI. Fluorination of X over CoF3 at 200° gave 90% yield of XI, whereas fluorination of VII resulted in complete substitution of the iodine. II (2 g.) in 50 ml. Et2O at -55° treated dropwise with stirring with N MeLi (from MeBr) and the soln. **stirred** 30 min. at -55°, **stirred** with addn. of 6 g. Br and the mixt. **stirred** 30 min. at -55° and at 20° 1 hr., dild. with 10 ml. H2O and treated with Na2S2O3, the washed and dried filtered Et2O soln. evapd. and the residue (3.4 g.) sepd. by chromatography on unit B yielded 1.7 g. XI, m. 109-10°. II (1 g.) in 50 ml. Et2O at -55° **stirred** with dropwise addn. of 0.93N MeLi (from MeBr) and the mixt. **stirred** 30 min. at -55°, bubbled through 30 min. with MeBr at -55° and at 25-30° 30 min., the soln. refluxed gently 30 min. and the cooled, washed and dried soln. freed from Et2O and excess MeBr, the residue (1.7 g.) sepd. on column B from 1.0 g. Et2O and gave 0.5 g. IX, m. 125.5-6.5°,

together with a trace of X. The same starting mixt. without passage of MeBr gave 1.8 g. residue, sepd. chromatographically to yield (from 1 g. II), 0.1 g. IX and 0.5 g. X. Further evidence for the operation of the proposed mechanism was provided by decompn. of the Li salt of IV in the presence of furan. II (3 g.) in 50 ml. Et2O at -55° **stirred** with dropwise addn. of 0.93N MeLi (from MeBr) and **stirred** 30 min. at -55°, **stirred** with dropwise addn. of 10 ml. redistd. furan and the mixt. **stirred** 30 min. at -55° and kept 30 min. at 25-30°, the system **stirred** 1 hr. under gentle reflux and the filtered soln. freed from Et2O, sepd. by vapor phase chromatography and the 1.6 g. waxy adduct (XII) analyzed by chromatography on unit B column showed the presence of 2 roughly equal components, m. 70-90°, m/e 343, 66, τ 6.5 s, 5.3 s, 6.4 m, 5.1 m, ν 1300-1200 cm.-1 (KBr). The formation of 2 closely similar structures would be expected from Diels-Alder addn. of furan to a bridgehead olefin.

CC 34 (Alicyclic Compounds)

L36 ANSWER 21 OF 32 HCA

61:87798 Original Reference No. 61:15304a-c Nitric phosphate fertilizers. (Asahi Chemical Industry Co., Ltd.). GB 970946 19640923, 8 pp. (Unavailable). PRIORITY: JP 19601005.

AB In the process for the manuf. of fertilizers by digesting phosphate rock with a mixt. of HNO3 and H2SO4 or K2SO4, ammoniating the reaction mixt., and drying, an improvement comprises conducting the digestion in 2 stages, thereby permitting regulation of the Ca:SO42- ratio so that the byproduct gypsum is produced in readily filterable form and the viscosity remains low. For example, 60% HNO3 1933, and K2SO4 716 kg./hr, were continuously mixed, and the mixt. was fed to a 1st digestion stage concurrently with 450 kg./hr, phosphate rock. The Ca in the rock was equiv. to the SO42- in the acid mixt. The temp. was 45° and the retention time was 30 min. The slurry **flowed** to a 2nd digestion stage where an addnl. 468 kg./hr. phosphate rock was added. The temp. was 50° and the retention time was 45 min. The slurry from the 2nd stage contained gypsum crystals 50-300 μ long, and the viscosity was 0.5-1.5 poises. Ammoniation was then carried out to pH 3.2, and the slurry was concd. to 10% H2O; the viscosity at this stage was 35 poises (100°, 20 **r.p.m.**). Granulation and drying yielded a **product** contg. total **P2O5** 10.69, H2O-sol. **P2O5** 3.01, N 13.9, K2O 12.1, CaO 15.99, SO3 10.47, and H2O 1.5%. As an alternate procedure the gypsum can be filtered out before ammoniation. Brit. 970,947; 7 pp. In the process of the preceding abstr. a portion of the slurry or filtrate from the 2nd digestion is recirculated to the 1st digestion, thereby aiding the growth of gypsum crystals.

IC C01B

CC 73 (Fertilizers, Soils, and Plant Nutrition)

L36 ANSWER 22 OF 32 HCA COPYRIGHT 2004 ACS on STN
60:68186 Original Reference No. 60:11995e-h,11996e-f Oxygen isosteres of carcinogenic hydrocarbons. I. Synthesis of benzobis(benzofurans). Dingankar, P. R.; Gore, T. S. (Univ. Bombay). Indian Journal of Chemistry, 2(2), 71-3 (Unavailable) 1964. CODEN: IJOCAP. ISSN: 0019-5103.
GI For diagram(s), see printed CA Issue.
AB The title compds. were synthesized for study of their carcinogenic activity. A soln. of 10 g. 2,5-dichlorohydroquinone in 100 ml. abs. MeOH was added to a soln. of 2.6 g. Na in 50 ml. abs. MeOH, the mixt. refluxed 15 min., and the alc. removed in vacuo to give 2,5-dichlorohydroquinone Na salt (I). 2-Bromocyclohexanone (II) (21 g.) and 200 ml. dry C6H6 were added to I and the **mixt.** shaken **mech.** 72 hrs. under N. Addn. of 30 ml. 2% aq. NaOH gave 13 g. 1,4-bis(2-oxocyclohexyloxy)-3,6-dichlorobenzene (III), m. 236° (2,4-dinitrophenylhydrazone m. 242°). A mixt. of 10 g. **P2O5** and 20 ml. phosphoric acid (d. 1.7) was heated 1 hr. at 200° and cooled, 1 g. III added, and the mixt. **stirred** 3 hrs. at 100° and poured into 100 g. crushed ice to give 0.7 g. 6,12-dichloro-1,2,3,4,7,8,9,10-octahydrobenzo[1,2-b:4,5-b'] bis(benzofuran) (IV), m. 241-2°. IV (0.16 g.) and 0.12 g. Pd-C (10%) was heated 1.5 hrs. at 200° and then 4 hrs. at 280-300°. The product sublimed in the condenser was benzo[1,2-b:4,5-b']bis(benzofuran) (IVa) (0.1 g.), m. 267-8°. Similarly, condensation of the di-Na salt of 2,3-dichlorohydroquinone (from 5 g. of the dichlorohydroquinone) with 10.5 g. II by shaking 72 hrs. in dry C6H6 gave 6 g. 1,4-bis(2-oxocyclohexyloxy)-2,3-dichlorobenzene, m. 250° (BuOH), which on cyclodehydration (as for IV) gave 6,7-dichloro-1,2,3,4,9,10,11,12-octahydrobenzo[1,2-b:4,3-b']bis(benzofuran) (V), m. 299-300° (BuOH). V (0.2 g.) on heating 5 hrs. with 0.15 g. Pd-C (10%) at 320-40° under N gave benzo[1,2-b:4,3-b']bis(benzofuran) (Va), m. 139° (BuOH). Similar condensation of the di-Na salt of 4-chlororesorcinol (from 7.5 g. 4-chlororesorcinol) with 18 g. II gave 7 g. of the dioxo compd., which failed to crystallize, but which, in Me2CO and CHCl3 refrigerated several days, gave 1,3-bis(2-oxocyclohexyloxy)-4-chlorobenzene, m. 157°, which on cyclodehydration (as for IV) gave 2 g. 6-chloro-1,2,3,4,8,9,10,11-octahydrobenzo[1,2-b:3,4b']bis(benzofuran) (VI), m. 154° (BuOH). Finally, dehydrogenation of 0.5 g. VI with 0.25 g. Pd-C (10%) (as in IV) gave 0.3 g. benzo[1,2-b:3,4-b']bis(benzofuran) (VIa) m. 164-5° (BuOH). Similarly, 6,12-dimethylbenzo [1,2-b:4,5-b']bis(benzofuran) (VII), m. 254° (obtained by C6H6 extn.), and 6,12-dimethylbenzo[1,2b:5,4-b']bis(benzofuran) (VIII), m. 174° (BuOH) were synthesized from 2,5-dimethylhydroquinone

and 2,5-dimethylresorcinol, resp. In these 2 cases, however, the oxo compds. were unstable and could not be isolated. The products of condensation were the cyclized compds. 6,12-dimethyl-1,2,3,4,7,8,9,10-octahydrobenzo[1,2-b:4,5-b']bis(benzofuran), m. 262° (BuOH) and 6,12-dimethyl-1,2,3,4,8,9,10,11-octahydrobenzo [1,2-b:5,4-b']bis(benzofuran), m. 192° (BuOH), resp., which on dehydrogenation gave VII and VIII in excellent yields.

CC 38 (Heterocyclic Compounds (More Than One Hetero Atom))

L36 ANSWER 23 OF 32 HCA COPYRIGHT 2004 ACS on STN

59:44696 Original Reference No. 59:8090b-d Nitrogen-containing superphosphate. Ch'en, Wei-Ts'ang Huaxue Tongbao (No. 8), 38-42 (Unavailable) 1960. CODEN: HHTPAU. ISSN: 0441-3776.

AB Hair is washed with water and slowly immersed in 60%, H_2SO_4 (1 kg./kg, hair), heated at 90°, and **stirred** for 10 min. to a black liquid consisting of a mixt. of various amino acids and excess H_2SO_4. Fresh bones are ground to a particle size of about 5 mm., placed in a kettle with water and are heated under 1.5-2 atm. pressure in the kettle; the resultant glue is from time to time replaced by water. Then the bones are dried and milled. The bone meal is mixed with the black liquid obtained, and the mixt. is heated at 70° in a Beskov chamber for 20 min. After cooling, the superphosphate formed is cut out in the usual manner. The product, contg, amino acids, $Ca(H_2PO_4)_2.H_2O$, $CaSO_4$, and $CaSO_4.1/2H_2O$, is a dark gray powder having a pleasant odor and is stable on prolonged storage. Chem. compn. of the **product** (in %) assimilable **P_2O_5** $\geq$ 18, N $\geq$ 8; moisture $\leq$ 15, free acidity $\leq$ 5.5. The dil. soln. of glue obtained as a by-product can be hydrolyzed with H_2SO_4 like the hair, or evapd. to get a glue, in which case the supernatant fatty layer of liquid must be first removed. The method of analysis is described.

CC 73 (Fertilizers, Soils, and Plant Nutrition)

IT Water, analysis
(detn. in free-**flowing** powders)

IT Powders
(free-**flowing**, water detn. in)

L36 ANSWER 24 OF 32 HCA COPYRIGHT 2004 ACS on STN

57:42519 Original Reference No. 57:8429i,8430a-i,8431a-i,8432a-e Dinitroacetonitrile. II. Derivatives of dinitroacetonitrile from Michael, Mannich, and alkylation reactions. 2,2-Dinitro-2-cyanoethanol and its derivatives. Parker, Charles O.; Emmons, William D.; Pagano, Angelo S.; Rolewicz, Henry A.; McCallum, Keith S. (Rohm & Haas Co., Huntsville, AL). Tetrahedron, 17, 89-104 (Unavailable) 1962. CODEN: TETRAB. ISSN: 0040-4020.

AB Addn. of $HC(NO_2)_2CN$ (I) to carbonyl conjugated unsatd. systems was a

generally successful reaction for the prepn. of Michael adducts. I tetrahydrate (II, 24.0 g.) and 17.2 g. H2C:CHCO2Me heated 5 hrs. at 50° in 35 ml. MeOH, kept 16 hrs. at 20°, the volatile material evapd. in vacuo, the residue taken up in Et2O, the washed and dried soln. evapd., and the residual liquid (8.4 g.) flash distd, at 100-20°/0.05 mm. yielded 21% distillate, redistd. to give a sample of (O2N)2C(CN)CH2CH2CO2Me (III), b0.12-0.15 78-80°, n2D 1.4595. III (1.2 g.) refluxed 3 hrs. in 15 ml. 20% HCl and the solid product (91%) recrystd. from H2O (C) yielded (CH2CO2H)2 m. 186-9°. NaC(NO2)2CN (12.5 g.) in 250 ml. Et2O **stirred** 30 min. with dropwise addn. of 4.2 g. H2SO4 at 20°, the filtered soln. treated with 5.8 g. recrystd. H2C: CHCONH2 together with some EtOAc, the soln. refluxed 24 hrs., the filtered soln. evapd., the partially cryst. residue (12 g.) taken up in alc., and the filtered soln. dild. with C6H6 gave 5.9 g. material, m. 43-5% recrystd. 3 times from CHCl3-alc. to give 29% (O2N)2C(CN)CH2CH2CONH2, m. 62-3°. II (28.5 g.) and 14.5 g. H2C:CHCO2H (IV) kept 48 hrs. at 25-35° in 15 ml. H2O, the volatile material evapd. in vacuo, the solid (29.6 g., m. 95-112°) recrystd. from 1:1 CHCl3-C6H6, and the cryst. material (60%, m. 104-9°) recrystd. 4 times from Et2O-CHCl3 (C) gave (O2N)2C(CONH2)CH2CH2CO2H (V), m. 115-17°. The filtrate from the CHCl3,-C6H6 crystn. evapd. and the product fractionated yielded 13% (O2N)2C(CN)CH2CH2CO2H, m. 73-4° (CHCl3). IV (40 g.) and 8.0 g. II kept 14 hrs. in 11 ml. Me3COH, the solvent evapd. in vacuo, the residue triturated with CHCl3, and filtered yielded 69% slightly impure V, m. 111-13°. NaC(NO2)2CN (10.0 g.) in 80 ml. EtOAc **stirred** 30 min. with dropwise addn. of 3.3 g. H2SO4 at 20°, the filtered soln. kept 12 hrs. at 40° with 5.0 g. IV, the solvents removed in vacuo, and the residue (15 g.) extd. with Et2O and CHCl3 yielded 34% α,α-dinitroglutarimide (VI), recrystd. from H2O and twice from EtOAc-C6H12 to give a sample, m. 146-8°, v 3160, 3060, 1578 cm.-1 V (0.7 g.) in 30 ml. MeCN **stirred** 2 hrs. with excess **P2O5** (exothermic reaction), the solvent evapd., the residue extd. with Et2O, and the product (46%, m. 148-50% recrystd. from EtOAc-CHCl3 gave VI, m. 150-1°. II (9.2 g.) kept 40 hrs. in 10 ml. H2O contg. 2.8 g. H2C:CHCHO, the oily layer (96%) taken up in 30 ml. MeOH, refluxed 5 hrs. with 9.4 g. HC(OMe)3 and 0.08 g. p-MeC6H4SO3H.H2O, and the volatile material evapd. in vacuo gave 66% yellow liquid, distd. to yield 57% (O2N)2C(CN)CH2CH2CH(OMe)2, b0.4 80-1°. The adduct from another run flash distd. yielded 31% impure (O2N)2C(CN)CH2CH2CHO, b0.75-1.30 80-92°. The diversity of products from IV was accounted for most readily by postulating cyclization of the normal adduct. II (0.044 mole) **stirred** 15 hrs. at 35-40° in 250 ml. MeOH with 0.016 mole recrystd. 1,3,5-triacryloylperhydro-s-triazine, the solvent evapd., the residue taken up in alc., and

dild. with CHCl3 yielded 26% 1,3,5-tris(γ,γ,-dinitro-γ-cyanobutyryl)perhydro-s-triazine, m. 143 5°. II (0.123 mole) **stirred** 7 hrs. at 55° with 0.065 mole recrystd. methylenebisacrylamide in 300 ml. H2O, most of the solvent evapd. in vacuo, the residue taken up in a min. of alc., and dild. with H2O yielded 31%[(O2N)2C(CN)CH2CH2CONH]2CH2, m. 134-5° (aq. alc.). MeCOCH:CH2 (5.0 g.) and 12.0 g. II in 15 ml. H2O kept 5 days at 20°, the oily layer (92.5%) washed 3 times with 35 ml. H2O, taken up in Et2O, the dried (MgSO4) soln. evapd., the residue flash distd. at 100-4°/0.5-1.0 mm. to give 68% distillate, n20D 1.4650, and redistd. through a falling film still at 77°/0.2-0.5 mm. gave 5,5-dinitro-5-cyano-2-pentanone, n20D 1.4646, v 2245, 1721, 1599, 1297 cm.-1; semicarbazone m. 137-8° (decompn.) (aq. alc.). Under rather limited environmental conditions, N-(2,2-dinitro-2-cyanoethyl)amides were prepd. through the reaction of I with N-methylolamides. In all expts. I was used as obtained by neutralizing NaC(NO2)2CN in EtOAc with an equiv. of H2SO4, stirring the mixt. 30 min., and using the filtered soln. BzNHCH2OH (5.0 g.) in 30 ml. EtOAc **stirred** 2 hrs. at 50° with dropwise addn. of 0.033 mole I in 50 ml. EtOAc, the mixt. kept 30 min. at 50° the cooled mixt. freed from volatile material in vacuo, the residue extd. with CH2Cl2, the filtered ext. evapd., and the residue (20%, m. 117-18°) recrystd. from CCl4 and twice from C6H6 gave BzNHCH2C(NO2)2CN, m. 119.5-20.5°. AcNHCH2OH (8.1 g.) in 30 ml. EtOAc **stirred** with 0.09 mole I in EtOAc and 5 g. anhyd. MgSO4, the soln. warmed to 30° kept 2 hrs., the filtered soln. evapd. in vacuo, the residue shaken with 2-3 vols. ice H2O, decanted, the residue taken up in Et2O, the dried soln. evapd., and the product (5.5 g., m. 70-3°) recrvstd, from C6H6 gave AcNHCH2C(NO2)2CN, m. 76.5-7.5°. MeCH:CHCONH2 (4.25 g.) and 1.5 g. paraformaldehyde ground together with addn. of 2 drops of nearly satd. aq. K2CO3, grinding continued 2-3 min., the mixt. heated to 50-60° with stirring, the cooled mixt. taken up in 40 ml. dioxane, the filtered soln. **stirred** with addn. of 14 g. powd. Drierite, **stirred** 2 hrs. at 40-5° with dropwise addn. of 0.05 mole I in 50 ml. EtOAc, the mixt. kept 30 min. at 40-5°, the cooled filtered soln. freed from volatile material in vacuo, the viscous residue triturated in ice H2O, and the dried solid (3.3 g., m. 70-3°) recrystd. from C6H6 yielded 27% MeCH:CHCONHCH2C(NO2)2CN, m. 74-5°. Similarly, 0.05 mole H2C: CHCONH2 gave 20% H2C: CHCONHCH2C(NO2)2CN, m. 77-8° (C6H6). (HOCH2NH)2CO (0.11 mole) and 0.075 mole anhyd. MgSO4 **stirred** 5 hrs. at 12° with dropwise addn. of 0.22 mole I in EtOAc, the residue on evapn. of the filtered soln. triturated with cold H2O, the dried product extd. with Et2O, the product (1.5 g., m. 127°) extd. with boiling ClCH:CHCl and boiling Cl2CHCH2Cl, the residue taken up in Et2O, and the soln.

dild. with petr. ether gave OC[NHCH2C(NO2)2CN]2, m. 136°. Formalin (250 ml., 37%) treated portionwise with 76.5 g. NaC(NO2)2CN, **stirred** 30 min. with dropwise addn. of 27.8 ml. chilled concd. H2SO4 at 23-6° (ice bath), the mixt. kept 4 days at 20°, and extd. 4 times with 50 ml. Et2O yielded 95% HOCH2C(NO2)2CN (VII), n20D 1.4470. (CF3CO)2O (0.113 mole) and 1.0 g. β-C10H7OH treated dropwise at 30° (ice bath) with 0.113 mole anhyd. **MeCH**:CHCO2H, the **mixt.** **stirred** 5 min., **stirred** at 20-30° with dropwise addn. of 0.087 mole VII, the mixt. **stirred** 1 hr., poured into 500 ml. ice H2O, extd. with 200 ml. Et2O, the mixt. neutralized with solid Na2CO3, the aq. layer extd. twice with 50 ml. Et2O, the combined washed and dried Et2O soln. evapd., and the ester (79%) flash distd. yielded 32% MeCH :CHCO2CH2C(NO2)2CN, b0.07 53-8°, v 2260, 1740, 1602 cm.-1 Similarly, 0.13 mole (CF3CO)2O, 0.13 mole AcOH, and 0.10 mole VII yielded 57% acetate, distd. in vacuo to give 34% product, b1.0 71-92°, fractionated to yield 26% pure AcOCH2C(O2N)2CN, b1.25 73-5°, n20D 1.4439, d20 1.335. CHCl3 (50 ml.), 3.5 g. VII, 1.3 g. AlCl3, and 1.0 g. (p-HOC6H4)2NH **stirred** at 24-7° (cooling) with addn. of 1.8 g. H2C:CHCOCl, the mixt. heated 1 hr. at 30-5° and 1 hr. at 35-40° with rapid evolution of HCl, the cooled mixt. poured into 500 ml. ice H2O, the aq. layer extd. with 300 ml. CHCl3, the filtered CHCl3 washed with 1% aq. NaHCO3, and the dried soln. evapd, in vacuo gave 3.2 g. product, distd. to yield 49% H2C:CHCO2CH2C(O2N)2CN, b0.1 56-60°, v 1750, 1600 cm.-1 Concd. HNO3 (42 g.) and 63 g. concd. H2SO4 treated dropwise at 0-5° (ice salt bath) with 300 ml. and twice with 50 ml. Et2O, the Et2O washed with 50 ml. 1% aq. NaHCO3 and 3 times with 50 ml. H2O, and the dried soln. evapd. yielded 67% product. Distn. of a sample in vacuo gave the nitrate ester, b0.1 46-55°, v 1600, 1678 cm.-1, becoming acidic fairly rapidly on standing. (CF3CO)2O (25 g.) refluxed with gradual addn. of VII, the soln. heated 1 hr. at 55°, kept overnight, volatile material evapd. in vacuo, the residue distd. over 0.2 g. ethyl centralite, and the fractions (11.3 g.), b0.04-0.06 33-8°, and (1.6 g.) b0.05-0.08 32-9°, combined and redistd. yielded 36.6% CF3CO2CH2C(O2N)2CN, b0.15 39°, n20D 1.4045, v 2260, 1812, 1610 cm.-1 VII (42.0 g.), 53.5 g. AlCl3, and 1.5 g. Cu2Cl2 **stirred** in 1 l. CHCl3 at 18-23° with addn. of 25.1 g. **MeCH** :CHCOCl, the **mixt.** heated 5 hrs. at 50-60°, treated with 1.5 g. Cu2Cl2, heated 7 hrs. at 50-60°, the cooled filtered soln. poured into 2400 ml. H2O, the aq. layer washed 4 times with 150 ml. CHCl3, the CHCl3 washed 4 times with 100 ml. 5% aq. NaHCO3, and the residue on evapn. (24.2 g.) flash distd. gave 51% product, b0.17 62-4°, n20D 1.4573, redistd. to yield 47% MeCH:CHCO2CH2C(NO2)2CN, b0.07-0.10 59-62°, n20D 1.4582, d20 1.174. KOH (1.28 g.) in 15 ml.

anhyd. MeOH treated dropwise with 2.5 g. NC(O2N)2CCH2CH2CO2Me gave 1.9 g. (O2N)2CHCH2CH2CO2Me K salt, m. 160-1°. The salt (11.5 g.) in 300 ml. H2O neutralized with H2SO4, the aq. layer extd. 6 times with 200 ml. Et2O, the combined org. layers washed 5 times with 100 ml. H2O, and the dried soln. evapd, gave 5.4 g. product, purified by redistn. to give (O2N)2CHCH2CH2CO2Me, b0.03 46-7°, n20D 1.4554. The corresponding Na salt (4.28 g.) in 10 ml. H2O treated with 1.70 g. H2C:CHCO2Me and kept 24 hrs., extd. 4 times with 50 ml. Et2O, and the product (2.4 g., m. 43-5°) recrystd. from alc. (C) yielded 40% snowwhite (O2N)2C(CH2CH2CO2H)2, m. 45.5-6.0°. Reactions of the dinitrocyanomethide ion with org. halides gave products, which represented covalent bond formation derived from all 3 possible contributing structures [:-C(CN)(NO3)2, O2N(CN)C: N(O)O-:, (O2N)2C:C:N:-] of the ion. Only Me, H2C:CHCH2, and Me3C halides gave stable isolable products. AgC(NO2)2CN (28.7 g.) in 300 ml. MeCN heated 3 hrs. at 40-5° with 18.0 g. H2C:CHCH2Br, filtered from 9.2 g. AgBr, the mixt. heated 4 hrs. at 40-60° with 2 g. H2C:CHCH2Br, the filtered soln. kept 2 days with 2 g. H2C:CHCH2Br, the filtered soln. evapd., the residue taken up in Et2O, the washed and dried soln. evapd., and the residue (10.4 g.) flash distd, gave 35% material, n20D 1.4558, fractionated through a Holtzman column to give 3.5 g. pure H2C:CHCH2C(NO2)2CN, b0.4 38-40°, n20D 1.4552. Me3CBr (55.0 g.) **stirred** (cooling bath) with addn. of 9.6 g. AgC(NO2)2CN, the mixt. **stirred** 2 hrs. at 20°, dild. with 200 ml. Et2O, kept overnight, the soln. extd. 3 times with 250 ml. 5% NaOH, the Et2O washed, dried, evapd., and the oily residue sublimed yielded 17% Me3CC(NO2)2CN (VIII), m. 120-4°, v 1595 cm.-1 The alk. ext. acidified with H2SO4 and the liberated amide crystd. from warm aq. MeOH yielded 18% (O2N)2CHCONHCMe3, (IX), m. 110-11° (decompn.). II (16.4 g.) and 12.4 g. NaC(NO2)2CN in 39.3 g. Me3COH **stirred** 20 hrs. at 60°, the cooled mixt. dild. with Et2O, the lower aq. layer extd. with Et2O, the combined solns. evapd. in vacuo, the oily residue extd. with petr. ether, the insol, residue taken up in Et2O, the ext. washed with 5% aq. NaHCO3, and the alk. washings acidified gave 1.2 g. material, m. 99-100°. The petr. ether ext. washed with 5% aq. NaHCO3 and the ext. acidified gave 0.3 g. similar material, combined (9.1%) and recrystd. from dil. MeOH to give IX, in. 110.5-11.0° (decompn.). The washed ext. concd. and cooled to -70° yielded 13.6% material, m. 120° (decompn.), recrystd. from alc. to give VIII, m. 132-3° (decompn.). NaC(O2N)2CN (15.3 g.) in Et2O treated dropwise with H2SO4, the filtered soln. treated with 200 ml. Me3COH and 15 g. H2SO4 24 hrs. at 50°, the volatile material removed, the H2O-washed product taken up in Et2O, the washed and dried soln. evapd., the MeOH-washed residue (11.0 g.) taken up in warm C6H6, dild. with petr. ether, filtered from pptd. IX, the filtrate evapd., and the residue freed from VIII by extn.

with petr. ether gave 1.3 g. solid, m. 162-5°, recrystd. to give (O2N)(C(CN):N(O)OCMe3, m. 164-5°. MeI (250 g.) **stirred** 15 min. with addn. of 41.8 g. AgC(NO2)2CN, the mixt. **stirred** 1 hr. at 20°, dild. with 250 ml. Et2O, and filtered after 1 hr. gave 14.9 g. O2NC(CN):N(O)OMe (X), m. 62-4° (H2O), identified from a study of hydrolysis products in acidic and basic solns. and by the strong ultraviolet absorption band at 300 mμ.

CC 27 (Aliphatic Compounds)

L36 ANSWER 25 OF 32 HCA COPYRIGHT 2004 ACS on STN

53:50960 Original Reference No. 53:9137g-i,9138a-b Kinetics of the reaction between a vinyl fluoride and sodium ethoxide. Silversmith, Ernest F.; Smith, Doris (Mount Holyoke Coll., South Hadley, MA). Journal of Organic Chemistry, 23, 427-30 (Unavailable) 1958. CODEN: JOCEAH. ISSN: 0022-3263.

AB Ph2C:CHF (I), treated with NaOEt in alc. at 99.75°, was converted by an addn.-elimination reaction to Ph2C: CHOEt (II) at a rate 270 faster than the conversion of Ph2C:CHCl (III). BrCH2CO2Et (110 g.) and 129 g. anhyd. KF processed according to Bacon, et al. (C.A. 42, 8777e), and the **mixt. stirred mechanically** yielded 15.0 g. FCH2CO2Et (IV). Decanted PhMgBr (10.0 g. Mg and 30.0 g. PhBr in 200 ml. Et2O) treated in 1 hr. with 6.1 g. IV in 200 ml. Et2O with stirring at -65 ± 10° (solid CO2Me2CO bath) in an N atm., the mixt. **stirred** slowly at -11° with 15 g. NH4Cl in 200 ml. H2O, the dried (Na2SO4) Et2O layer evapd., and the residue fractionated yielded 41% FCH2CPh2OH (V), m. 71.8-2.6°. V (1.55 g.) in 50 ml. dry C6H6 refluxed 2.75 hrs. with 1.59 g. **P2O5**, the decanted soln. evapd., and the residue distd. gave 0.83 g. I, b2 102-3°, oxidized with alk. KMnO4 to Ph2CO, identified through the 2,4-dinitrophenylhydrazone, m. 240°. PhMgBr (17 g. Mg and 85 g. PhBr in 150 ml. Et2O) added dropwise with stirring at 0° to 20 g. ClCH2CO2Et in 200 ml. Et2O, the mixt. dild. with 200 ml. ice-water, the H2O-washed and dried (MgSO4) Et2O layer fractionated, and the distillate, b2 140°, recrystd. (C6H14) gave 9.0 g. ClCH2CPh2OH (VI), m. 63.4-5.0°. VI (6.4 g.) and 6.0 g. **P2O5** refluxed 1 hr. in 50 ml. dry C6H6 and the mixt. distd. yielded 70% III, b5 138-9°, oxidized to Ph2CO. For rate detns. weighed samples of I or III dild. with alc. NaOH at 25° were heated at 99.75 ± 0.05° in ampuls and the NaOEt concns. detd. periodically by titration of 5 ml. aliquots with standard HCl against phenolphthalein. I(3.0 g.) in 70 ml. 0.64M NaOEt in alc. heated 118 hrs. at 99.75°, the mixt. dild. with 500 ml. H2O, extd. 4 times with 100 ml. Et2O, the ext. evapd., and the residue distd. gave III, b2 136-8°, oxidized to Ph2CO. The suggested addn.-elimination mechanism was discussed.

CC 10E (Organic Chemistry: Benzene Derivatives)

L36 ANSWER 26 OF 32 HCA COPYRIGHT 2004 ACS on STN
52:103947 Original Reference No. 52:18253g-i,18254a-i,18255a-e
Flourocyclohexanes. III. cis-1H,4H-trans-2H- and trans-1H,2H-cis-4H-Nonafluorocyclohexane and derived compds..
Godsell, J. A.; Stacey, M.; Tatlow, J. C. (Univ. Birmingham, UK).
Tetrahedron, 2, 193-202 (Unavailable) 1958. CODEN: TETRAB. ISSN: 0040-4020.

AB The nonafluorocyclohexanes (I, II), b. 92° and 101°, were dehydrofluorinated to give the same 6 compds. identified by oxidation and other studies as 3H,4H- and 4H,5H-octafluorocyclohexene (III, IV), 1H-1,4-, 1H-1,3-, and 2H-1,3-heptafluorocyclohexadiene (V, VI, VII), and C6H6, thus indicating a 1H,2H,4H-structure for the satd. precursors. Fractional distn. controlled by analytical gas chromatography of the partly fluorinated cyclohexane mixt., b. above 91.7° (C.A. 51, 3472e), gave I, b. 92.0-2.5°, m. 44-6°, a mixed intermediate fraction, and II, b. 101°, m. 12-14°, nD14 1.3194, in 10 and 5% yields of the original polyfluoride mixt. I (11.0 g.) refluxed 6 hrs. with 10.0 g. KOH in 10 ml. H2O and the org. phase (9.0 g.) sepd., washed with H2O and dried (MgSO4), the mixt. sepd. in a 16 ft. + 3 cm. tube packed with 1:2 dionyl phthalate-kieselguhr at 80° with 10 l./hr. N **flow**, and each fraction distd. in vacuo gave 0.18 g. V, b. 66.5-67°, nD18 1.3275, 1.37 g. VI (or VII), b. 71.5-2.5°, nD18 1.3400, 0.51 g. VII (or VI), b. 76°, nD18 1.3383, 0.46 g. C6F6, b. 80°, nD18 1.3746, 3.75 g. III, b. 85°, nD18 1.3277, 2.51 g. IV, b. 90°, nD18 1.3283. The conjugated dienes VI and VII were unstable with evolution of HF and the decompn. was retarded by storage at 0° in tightly closed vessels. V (1-12 g.) shaken 14 hrs. in an autoclave at 20° with 10 g. KMnO4 in 50 ml. H2O and the mixt. heated 4 hrs. at 100°, the product isolated according to T. and Worthington (C.A. 47, 1070c), and crystd. (Me2CO-CHCl3) gave 42% dianilinium difluoromalonate, m. 161-2°, and bis(S-benzylthiuronium) difluoromalonate, m. 184-6°. V showed v 1723, 1770 cm.-1 but no selective absorption in the range 240-300 mμ. Oxidation of VI (or VII) 17 hrs. at 100° with aq. KMnO4 and isolation as above gave 20% dianilinium tetrofluorosuccinate, m. 224-5°, and bis(S-benzylthiuronium) tetrafluorosuccinate, m. 189-90°. The diene (2.0 g.) and 1.5 g. Cl irradiated 18 hrs. with ultraviolet light in a sealed hard-glass tube and the mixt. poured into aq. Na2S2O5, the **product** dried (**P2O5**), and distd. gave 2.63 g. 1,2,3,4-tetrachloroheptafluorocyclohexane, C6HCl4F7, b. 197-9°. VI (or VII) gave bands at v 1682, 1743 cm.-1 and λ 254 mμ (ε 3720, alc.). Similarly, VII (or VI), v 1679, 1732 cm.-1, λ 262.5 mμ(ε 3070, alc.) was

oxidized and the product isolated as 49% dianilinium tetrafluorosuccinate, converted to the bis(S-benzylthiuronium) salt. Chlorination yielded 74% $C_6HCl_4F_7$, b. 184-5°. III (0.18 g., v 1749 cm.-1, no selective absorption between 240 and 300 mμ) was heated 16 hrs. at 85° with 15 g. $KMnO_4$ and 3 g. $NaHCO_3$ in 50 ml. H_2O in a rocking autoclave and the product worked up as usual to give 1.67 g. acidic solid, distd. (0.22 g.) at 160-70°/15 mm. onto a cold finger to give 0.18 g. hygroscopic DL-threo-2H,3H-hexafluoroadipic acid (VIII), m. 126-8°. The crude acid (0.29 g.) in H_2O at pH 4 treated with aq. S-benzylthiuronium chloride yielded 0.11 g. bis(S-benzylthiuronium) salt, $C_{22}H_{24}F_6N_4O_4S_2$, m. 226-7° (H_2O). The acid and its derivs. are unstable and attempts to prep. a dianilinium salt and a diamide failed. Chlorination of 1.97 g. III yielded 1.81 g. 1H,2H-3,4-dichlorooctafluorocyclohexane, $C_6H_2Cl_2F_8$, b. 143-4°. III (2.23 g.) refluxed 8 hrs. with 10 g. KOH in 10 ml. H_2O and the washed and dried ($MgSO_4$) org. layer sepd. (1.19 g.) by preparative scale gas chromatography yielded 0.72 g. VI (or VII), b. 72°, 0.26 g. VII (or VI), b. 76°, and 0.14 g. C_6F_6. VIII (1.0 g.) and 5.0 g $KMnO_4$ refluxed 22 hrs. in 30 ml. N KOH and the sapon. product worked up yielded 73% $(CF_2CO_2H)_2$, m. 112-14°; dianilinium salt, m. 225-6° ($Me_2CO-CHCl_3$). IV (2.16 g., v 1750 cm.-1, no selective absorption in the ultraviolet) oxidized at 100° without addn. of $NaHCO_3$ to an acidic solid (1.21 g.) and a portion (0.44 g.) distd. at 180°/15 mm. gave 0.37 g. hygroscopic DL-3H,4H-hexafluoroadipic acid (IX), m. 150-1°; dianilinium salt, m. 186-7° ($Me_2CO-CHCl_3$); bis(S-benzylthiuronium) salt, m. 227-8° (H_2O). IX (0.25 g.) and 0.5 ml. HFO_3S refluxed 2 hrs. in 10 ml. alc. and the mixt. poured into H_2O, extd. with Et_2O and the filtered dried ($MgSO_4$) ext. satd. 30 min. with NH_3, kept 15 hrs. at 10-15°, and evapd. gave 0.08 g. diamide, $C_6H_6F_6N_2O_2$, m. 206-7° (H_2O). Chlorination of IV yielded 54% 1H,2H-4,5-dichlorooctafluorocyclohexane, b. 138-9°. IV (6.0 g.) refluxed 12 hrs. with 10.0 g. KOH in 10 ml. H_2O and the washed and dried product (4.26 g.) sepd. by gas chromatography gave 1.66 g. V, 0.54 g. C_6F_6, and 174 g. IV. IX (1.19 g.) refluxed 19 hrs. with 5 g. $KMnO_4$ and 30 ml. N KOH and worked up gave 0.95 g. acidic solid (X); dianilinium salt, m. 164-5°. X (0.69 g.) distd. at 155°/15 mm. onto a cold finger yielded 0.61 g. $CF_2(CO_2H)_2$, m. 115-16°. IX (5.0 g.) in 100 ml. alc. and 15.5 g. l-brucine in 200 ml. alc. boiled and the filtered soln. evapd. at 15 mm., the residue taken up in 100 ml. hot H_2O and the soln. kept 3 days at 10-15°, filtered (mother liquor A), and the residue (5.61 g.) twice recrystd. (25-35 ml. H_2O) gave 3.87 g. less sol. diastereoisomeric dibrucine salt (XI), m. 250° (decompn.), [α]D20 -12.6° (c 2.05, alc.). Mother liquor A concd. and filtered (mother liquor B) and the cryst. residue recrystd.

(H2O) 5 times gave 1.51 g. XI. XI (51.03 g.) in 50 ml. warm H2O made faintly alk. with 0.025 N NaOH and filtered from pptd. brucine (95% recovery), the filtrate acidified with H2SO4 and extd. continuously with Et2O, and the dried (MgSO4) ext. evapd. yielded 1.08 g. acidic solid, distd. (0.94 g.) at 220-30°/15 mm. to give 0.56 g. l-IX, [α]D24 -17.5° (c 4.0, H2O); bis(S-benzylthiuronium) salt, m. 227-8° (H2O), [α]D24 -10.9° (c 1.28, MeOH). The mother liquor B concd. and the crude salt purified to const. rotation gave 3.15 g. more sol. diastereoisomeric dibrucine salt, m. 250° (decompn.), [α]D21 -1.94° (c. 2.05, alc.), neutralized (2.81 g.) to give 0.75 g. crude acid, distd. (0.60 g.) to 0.43 g. d-IX, [α]D22 16.6° (c 1.93, H2O); bis(S-benzylthiuronium) salt, m. 227-8° (H2O), [α]D24 9.0° (c 1.3, MeOH). II (45.0 g.) refluxed 6 hrs. with 75 g. KOH in 75 ml. H2O and the org. layer worked up and dried gave 31.5 g. product. Preparative scale gas chromatographic sepn. of 8.94 g. mixt. and vacuum distn. of the fractions gave 0.67, 2.03, 0.69, 0.81, 0.35 and 3.90 g. of V, VI (or VII), VII (or VI), C6F6, III, and IV, resp. Samples (1 g.) of I and II were shaken 30 min. at 45° with 10 ml. 2N KOH in sealed tubes and the products analyzed by gas chromatography over 1:2 dinonyl phthalate-kieselguhr at 77° with 1.0 l./hr. N **flow** and over 1:3 tricresyl phosphate-kieselguhr at 85° with 0.9 l./hr. N **flow.** I gave very little of the monohexenes and only traces of the dienes whereas more than 50% of II was decompd. with formation of considerable quantities of monohexenes but only small amts. of dienes. IV (5.02 g.) in 25 ml. Et2O added dropwise in 10 min. to 0.88 g. LiAlH4 **stirred** in 25 ml. Et2O at 0° and the mixt. kept 10 min., decompd. with 25 ml. H2O and 25 ml. 50% H2SO4 and the dried Et2O evapd. through a 1 ft. gauze-spiral packed column, the residue, b. above 34°, fractionated by gas chromatography, and the fractions distd. in vacuo gave 1-63 g. 1H,trans-4H,5H-heptafluorocyclohex-1-ene (XII), b. 103-4°, nD18 1.3503, v 1710 cm.-1 [over the range 650-3500 cm.-1 identical with the spectrum of a heptafluorocyclohexene obtained by dehydrofluorination of 1H,2H,4H,5H-octafluorocyclohexane, b. 119° (cf. Stephens and T., C.A. 51, 16322b)], and 1.64 g. mixt. of 2-hexafluorocyclohexenes, b. 117-19°. XII treated 17 hrs. with aq. KMnO4 and worked up gave 23% DL-3H,4H-hexafluoroadipate, m. 189-90°; bis(S-benzylthiuronium) salt, m. 226-7°. XII (2.92 g.) refluxed 2.5 hrs. with 4.5 g. KOH in 4.5 ml. H2O and the H2O-washed org. layer dried (MgSO4) gave on preparative-scale chromatography 0.16 and 0.05 g. hexafluorocyclohexa-1,4-dienes, 0.48 g. C6HF5, b. 89°, and 1.15 g. XII, with identical infrared spectra with those of the 4 analogous products from the dehydrofluorination of 1H,2H,4H,5H-octafluorocyclohexane, b. 119°. Infrared spectra

of all new compds. were measured and deposited in the Documentation of Molecular Spectra, issued by Butterworths. The complete stereochemistry of I and II was suggested by the dehydrofluorinations and confirmed by further fluorination to give the known decafluorocyclohexanes showing that I and II are cis-1Ha, 4He-trans-2Ha- and trans-1Ha,2Ha-cis-4Ha-nonafluorocyclohexane, resp.

CC 10D (Organic Chemistry: Alicyclic Compounds)

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52:34749 Original Reference No. 52:6177i,6178a-i,6179a-d The dinitrogen pentoxide-olefin reaction. Stevens, Travis E.; Emmons, William D. (Rohm & Haas Co., Huntsville, AL). Journal of the American Chemical Society, 79, 6008-14 (Unavailable) 1957. CODEN: JACSAT. ISSN: 0002-7863.

AB Abs. HNO3 (100 g.) dehydrated with **P2O5** and the **product** sublimed in ozonized O gave 45-50 g. N2O5 (I) which was trapped and stored at -78°. Solns. of I were prepd. by adding the solvent to the I at -78° and warming to -10 to 0°. I (0.353 mole) in 200 cc. dry CHCl3 added dropwise to 75 cc. cyclohexene in 100 cc. CH2Cl2 during 40 min. at about -30°, the mixt. kept 1 hr. at -10°, quenched with aq. NaHCO3, and the org. layer washed, dried, and evapd. gave 60.3 g. residue; a 28.8-g. portion dissolved in 50 cc. MeOH and cooled to -78° deposited 1.96 g. bis(2-nitrosocyclohexyl nitrate), m. 149° (decompn.) (EtOHCHCl3). Distn. of the residual mixt. gave 14-17% mixed nitrocyclohexenes, b0.4 40-4°, n20D 1.4821-1.4833. A 31.5-g. portion of the residue shaken with 50 cc. C6H6, and the C6H6 soln. chromatographed on silica gel yielded some pure cis- and trans-isomer of 2-nitrocyclohexyl nitrate (II). Oily nitronitrates (3.7 g.) from the cyclohexene-I reaction passed with C6H6 through silica gel, shaken with 100 cc. 5% aq. NaOH, kept overnight, the basic soln. decanted from insol. oil, added dropwise to excess cold 15% H2SO4, and the Et2O evapd. gave 1.4 g. residue yielding with an equal amt. of 2,4-(O2N)2C6H3NHNH2 2.02 g. solid deriv.; a 1.09-g. portion chromatographed on silica gel yielded 0.47 g. cyclohexenone deriv., m. 164-5°, and 0.35 g. 4-nitratocyclohexanone deriv., m. 150-1°. Mixed cis- and trans-II gave similarly 1.2 g. 2,4-dinitrophenylhydrazones from which no pure compd. could be isolated. I (0.100 mole) in 80 cc. CH2Cl2 added during 20 min. to 15 cc. cyclohexene and 19.2 g. Et4NNO3 (III) in 200 cc. CH2Cl2 at -20°, warmed to 0°, **stirred** 0.5 hr., quenched with aq. NaHCO3, and the org. layer worked up gave 7.8 g. 3-nitrocyclohexene, b0.5 50-2°, n20D 1.4837, b5 68°, n20D 1.4828, and 4.1 g. cis-II, b0.5 130°, n20D 1.4834, m. 32-3°. I (0.149 mole) in 100 cc. CH2Cl2 added slowly with stirring to 15 cc. C3H6 in 300 cc. CH2Cl2 at -20 to -30°, warmed to 0°, **stirred**

15 min., quenched with aq. NaHCO3, and the org. layer concd. in vacuo to 100 cc. and chromatographed on silica gel gave 2.1 g. **mixt.** of **MeCH**:CHNO2 (IV) and CH2:CHCH2NO2 (V), b20 36-40°, n20D 1.4338, 0.8 g. intermediate fraction, and 6.0 g. O2NCH2CH(ONO2)Me (VI), b0.3 60°, n20D 1.4461, also obtained, b0.1 50°, n20D 1.4462, from MeCH(OH)CH2NO2 and I. I (0.135 mole) added to excess C3H6 in 300 cc. CH2Cl2 contg. 28.8 g. III gave 1.4 g. nitroolefins, n20D 1.4326, 0.6 g. intermediate fraction, and 6.9 g. VI, n20D 1.4454. A similar run with 0.150 mole I, excess C3H6, and 19.2 g. III during 1 hr. at 0° yielded 2.9 g. nitroolefin, b40 76-8°, n20D 1.4334, and 1.5 g. trap residue, n20D 1.4306, contg. 0.3 g. IV and 0.7 g. V; the nitroolefin fraction consisted of 2.0 g. V and 0.5 g. IV; further distn. of the crude product gave 11.8 g. VI, n20D 1.4453. The aq. and NaHCO3 washes neutralized with dil. HCl and extd. with Et2O gave 1.2 g. residue not investigated further. MeCH(OH)CH2NO2 dehydrated with o-C6H4(CO)2O gave IV, b37 58°, n20D 1.4545. I (0.120 mole) and excess EtCH:CH2 gave 1.4 g. nitrobutenes, b5 34-6°, n20D 1.4398, and 5.6 g. EtCH(ONO)2CH2NO2 (VII), b0.4 60-2°, n20D 1.4467. I (0.097 mole) and excess EtCH:CH2 contg. 20.0 g. III gave 1.4 g. nitrobutenes, n20D 1.4404, and 4.2 g. VII, n20D 1.4470; redistn. of the nitrobutene fraction gave MeCH:CHCH2NO2 (VIII), b53 75°, n20D 1.4389. A similar run with 0.160 mole I and excess EtCH:CH2 during 1 hr. at 0° gave 3.8 g. forerun, b5 36-8°, n20D 1.4400, 1.0 g. intermediate cut, and 13.5 g. VII, b0.2 62°, n20D 1.4466; the forerun consisted of 2.85 g. VIII and 0.25 g. EtCH:CHNO2. EtCH(OH)CH2NO2 dehydrated with o-C6H4(CO)2O gave VIII, b37 72°, n20D 1.4563. I (0.150 mole) and 30 cc. Me2C:CH2 in 250 cc. CH2Cl2 contg. 20.0 g. III gave 5.3 g. O2NCH2CMe:CH2, b30 52-4°, n20D 1.4434, 1.7 g. intercut, and 7.9 g. Me2C(ONO2)CH2NO2, b0.4 62-4°, n20D 1.4500, also obtained, b0.4 60°, n20D 1.4487, from O2NCH2C(OH)Me2 and I. I (0.090 mole) in 66 cc. CH2Cl2 added with stirring to 10.0 g. III and 15 cc. trans-(MeCH:)2 in 100 cc. CH2Cl2 gave 1.9 g. mixed nitroolefins, and 7.1 g. threo-MeCH(NO2)CH(ONO2)Me (IX), b1.5 63°, n20D 1.4436. I (0.090 g.) and 15 cc. cis-(MeCH:)2 gave similarly 7.2 g. erythro isomer of IX, b1.5 60°, n20D 1.4462. PhCH2CH:CH2 and I gave a product showing no nitrate ester absorption; a 5.00-g. portion of the residue oxidized with H2SO4-Na2Cr2O7, gave 0.96 g. p-O2NC6H4CO2H, m. 230-2°. 1-Octene (10.9 cc.) and 6.2 cc. C6H6 in 125 cc. CH2Cl2 treated dropwise during 25 min. with 0.050 mole I in 34 cc. CH2Cl2 at -5°, **stirred** 15 min. at 0°, quenched with aq. NaHCO3, and the org. layer worked up gave a residue contg. 1.6 g. PhNO2. A similar run, but in the presence of 9.6 g. III, gave 10.0 g. residue contg. 0.17 g. PhNO2. threo-IX (1.50 g.), 0.15 g. PtO2, and 10 cc. AcOH hydrogenated at room temp. and 3 atm. during 24 hrs., filtered, evapd., and the residue kept

overnight with 5 cc. pyridine and 4 cc. Ac2O, evapd., dissolved in 9:1 CH2Cl2-EtOAc, and chromatographed on silica gel gave 1.28 g. dl-threo-MeCH(OAc)CH(NHAc)Me(X), m. 71-2.5° (C6H6-ligroine). erythro-IX (1.50 g.) gave similarly 1.45 g. (crude) dl-erythro-isomer of X, m. 50-2°. cis-II (2.00 g.) and 0.20 g. PtO2 in 10 cc. AcOH hydrogenated 4 hrs. at room temp. and 3 atm., filtered, evapd., and the residue treated with 25 cc. 6N HCl, evapd. in vacuo, dild. with 30 cc. C6H6, distd. to dryness, and recrystd. from C6H6-EtOH gave 0.70 g. cis isomer of 2-aminocyclohexanol (XI).-HCl, m. 184-5° (decompn.) (EtOH-C6H6); N-Bz deriv. of XI, m. 183-4°. The nitro alc. fraction from cyclohexene and I refrigerated slowly deposited trans-2-nitrocyclohexanol (XII), m. 46-7°. Iso-Pr2NH.HNO2 (17.8 g.) and 9.8 g. cyclohexene oxide in 75 cc. Me2SO **stirred** 18 hrs. at 65°, poured into H2O, extd. with Et2O, and the ext. worked up gave 3.3 g. XII, n20D 1.4837. XII (2.00 g.) hydrogenated in the usual manner gave 0.93 g. trans-XI.HCl, m. 174-5° (C6H6-EtOH). Cl(CH2)2CH(OH)Me (XIII) (16.4 g.), n20D 1.4430, and 29.0 g. NaI in 175 abs. EtOH refluxed 4 hrs., poured into H2O, extd. with Et2O, and the ext. worked up gave 6.6 g. unchanged XIII, b20 75-80°, n20D 1.4435, and 14.4 g. (crude) I(CH2)2CH(OH)Me (XIV), b10 76°, n20D 1.5343. XIV (14.6 g.) and 16.5 g. AgONO yielded 5.6 g. O2N(CH2)2CH(OH)Me (XV), b0.2 49°, n20D 1.4445. XV (4.3 g.) in 70 cc. CH2Cl2 treated at -30° with 0.042 mole N2O5 in CH2Cl2, warmed to 0°, and worked up in the usual manner gave 3.3 g. MeCH(ONO2)(CH2)2NO2, b0.2 66°, n20D 1.4522.

CC 10 (Organic Chemistry)

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51:81397 Original Reference No. 51:14689h-i,14690a-f Acetylenic compounds. LV. The preparation and properties of some polyacetylenic acids, and their derivatives. Jones, E. R. H.; Thompson, J. M.; Whiting, M. C. (Univ. Manchester, UK). Journal of the Chemical Society, Abstracts 2012-17 (Unavailable) 1957. CODEN: JCSAAZ. ISSN: 0590-9791. OTHER SOURCES: CASREACT 51:81397.

AB cf. C.A. 51, 6507e. 1,3-Heptadiyne (17.5 g.) (sic) in 35 cc. Et2O was added dropwise to EtMgBr (from 10 g. Mg) in Et2O, refluxed 1 hr., poured onto excess CO2 in an autoclave, and the complex decompd. with ice and 15% H2SO4 to give 13.5 g. 2,4-heptadiynoic acid, m. 73-5° (from light petroleum, b. 40-60°); Me ester (from CH2N2 or H2SO4 in MeOH), b0.01 50°, nD17.5 1.5131. Similarly was prepd. from 1,3-octadiyne, 40% 2,4-nonadiynoic acid, m. 32-7° (from pentane). 1,4-Dichloro-2-butyne (74 g.) was added with stirring to a suspension of NaNH2 in liquid NH3, Et2O and dried paraformaldehyde in Et2O added, after 1 hr. NH4Cl added, the NH3 evapd., the soln. filtered, the solid washed with Et2O, the filtrate and washings evapd. and dried, the residue extd. with light petroleum (b.

40-60°), and the ext. evapd. at 0.01 mm. at room temp. to give 47 g. red oil, nD20 1.521-1.522, which solidified, identified as 2,4-pentadiyn-1-ol (I). Distn. of this is hazardous. I (21 g.) in 170 cc. C6H6 was added with cooling to EtMgBr (from 17 g. Mg) in C6H6, after 40 min., 18 g. **MeCHO** added, the **mixt . stirred** 18 hrs., the complex decompd. with ice H2O, the C6H6 layer sepd. and the aq. layer continuously extd. with C6H6, the exts. dried and evapd., the residue dissolved in C6H6, and adsorbed on alumina giving 33% 2,4-heptadiyne-1,6-diol (II), b. 85° (bath temp.)/5 + 10-4 mm., m. 50-3° (from Et2O). Similarly, from I and EtCHO was prepd. 56% 2,4-octadiyne-1,6-diol (III), b0.02 100° (bath temp.), nD21 1.5370, λ 2310 A., ε 1050. II and pyridine treated with SOCl2 gave 35% dichloride (IV), b0.01 31°, nD19 1.5530, λ 2670, 2520, 2390, 2270 A., ε 1350, 2050, 1650, 1100. III treated likewise gave the dichloro compd. (V), b0.01 60°, nD23 1.5457, λ 2670, 2520, 2390, 2260 A., ε 1450, 2250, 1850, 1450 (plus 30% 1-chloro-6-octene-2,4-diyne, nD19.5 1.5703, λ 2890, 2830, 2730, 2650, 2540, 2535, 2400 A., E1cm.1% 320, 370, 500, 510, 380, 400, 260). V in Et2O was added during 10 min. to a suspension of NaNH2 in liquid NH3 cooled to -77° by addn. of liquid N, NH4Cl added, the soln. extd. with isobutane, the ext. evapd. in the presence of MgSO4, tetrahydrofuran added, and the soln. added to EtMgBr. Carbonation and purification gave 10% 2,4,6-nonatriynoic acid, decomp. 95° (from CH2Cl2). IV was similarly dehydrohalogenated and added to EtMgBr to give octa-2,4,6-triynoic acid monohydrate; Me ester, m. 53-6° (from light petroleum). Me hepta-2,4-diynoate (VI) and NH3 soln. were shaken 3.5 hrs. at 15° to yield 2,4-heptadiynamide (VII), m. 148° (from C6H6-EtOH). Me 2,4,6-octatriynoate likewise gave 2,4,6-octatriynamide, discolored at 85° (from tetrahydrofuran-CH2Cl2). VII (1.0 g.), sand, and **P2O5** was heated at 100-30°/0.01 mm. in a sublimation app. and the sublimate dissolved in C5H12 to give 400 mg. 2,4-heptadiynonitrile, m. -5°, nD22 1.5387. VI formed several adducts: with CH2N2 it gave Me 4-but-1-ynylpyrazole-3-carboxylate, m. 92-4° (from C6H6-light petroleum), λ 2405, inflections at 2435, 2615 A., ε 10,600, 10,400, 6600, ν 3200-3400, 1727, 2250 cm.-1; with piperidine VI gave Me 3-(1-piperidyl)hept-2-en-4-ynoate, b. 140° (bath temp.)/10-4 mm., nD17 1.5551, λ 2320, 3090 A., ε 6700 and 14,700, ν 2247, 1706, 1630 cm.-1; and with cyclopentadiene, Me 2,5-dihydro-2,5-endomethylene-6-but-1-ynylbenzoate, b0.01 71° (bath temp.), nD23 1.5335, λ 2915 A., ε 6220, ν 3070, 2245, 2215, 1707, 720 cm.-1 Ultraviolet absorption data are given for RC.tplbond.CC.tplbond.CCOX (R and X given): Et, OH; Bu, OH; Et, OMe; Et, NH2; Me2C(OH), OH. For R(C.tplbond.C)3COX: Me, OH; Et, OH; Me, OMe; Et, OMe; Me, NH2. For EtC.tplbond.CCN, Et(C.tplbond.C)2CN, and Et(C.tplbond.C)3CN.

CC 10 (Organic Chemistry)

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51:81209 Original Reference No. 51:14601c-i,14602a-g Nitrosoacylamines and diazo esters. XII. Carbonium rearrangement in the decomposition of alkyl diazo esters. Huisgen, Rolf; Ruchardt, Christoph (Univ. Munich, Germany). Ann., 601, 1-21 (Unavailable) 1956. OTHER SOURCES: CASREACT 51:81209.

AB cf. C.A. 49, 12335i. Reactions of primary alkyl amines with HNO2 with decompn. of the alkyl diazonium ion undoubtedly take place through the carbonium ion, the H shift leading from the primary to the secondary or tertiary alkyl group, in direct competition with the attack of the nucleophilic solvent. The extent of such isomerization in the decompn. of the alkyl diazonium ion within an ion-pair in a nonpolar solvent is difficult to predict. The concept of such oriented ion-pairs as intermediates ibid. 599, 183(1956)) offers a satisfactory explanation of the decompn. of covalent diazo esters and of the reaction of diazoalkanes with a carboxylic acid. The decompn. of alkyl diazonium ions in aq. media serves as a good approximation to the extreme case of carbonium substitution reactions, independent of the nature of the alkyl group. PrN(NO)Bz (I) (10.0 g.) in 100 cc. dry C6H6 heated to 55° with evolution of 60 millimoles N and **MeCH**:CH2, the **mixt.** treated with ice-cold NaOH, filtered, and worked up gave 77% PrOBz, b11 107°, together with 1.5 ± 0.3% iso-PrOBz (by infrared detn.). Similar decompn. of 20 g. I in 200 cc. MeCN at 55° yielded 62% PrOBz contg. 3.4 ± 0.6% iso-PrOBz. I (14.0 g.) in 40 cc. HCONMe2 added dropwise in 30 min. with vigorous stirring to 40 cc. H2O and 20 cc. HCONMe2 at 80° and worked up gave 9% PrOBz contg. 9% iso-PrOBz together with 46% PrOH contg. 32.7% iso-PrOH. The % yield of iso-PrOH rises with the increasing polarity of the solvent. EtCHN2 (II) (cf. Adamson and Kenner, C.A. 32, 1098) at 0°/350-400 mm. bubbled in N atm. through 4 cc. 70% HClO4 in 18 cc. H2O and 30 cc. HCONMe2, and the products worked up gave 16.0 millimoles PrOH contg. 28.1% iso-PrOH. Similarly, II at 0°/400 mm. was bubbled through 30 cc. HCONMe2, 20 cc. H2O, and 6 g. BzOH and gave 9.3 millimoles PrOH contg. 27.2% iso-PrOH together with 1.1 millimoles PrOBz contg. about 4.3% iso-PrOBz. PrNH2 (4.1 g.) in 14 cc. 70% HClO4, 18 cc. H2O, and 60 cc. HCONMe2 **stirred** 3 hrs. with dropwise addn. of 10 g. NaNO2 in 15 cc. H2O at 0° and worked up gave 23.3 millimoles PrOH contg. 30.8% iso-PrOH. The agreement in the yields of isomers supports the conception of a common intermediate for the 3 types of reaction. The occurrence of BzOPr in addn. to PrOH in the expts. in aq. media is attributed to the formation of an oriented alkyl diazonium ion-pair and a scheme summarizing the reactions in nonpolar and aq. media is given. PrNH2 (20.0 g.) in 200 cc. AcOH **stirred** 90 min. at 0° with portionwise

addn. of 69 g. powd. $NaNO_2$, the mixt. **stirred** 3 hrs. at 0° and 3 hrs. at 20°, the mixt. distd., the distillate (150 cc.) dild. with 300 cc. H_2O and distd., the org. phase sepd. and the neutralized aq. phase satd. with NACl at 0°, extd. 3 times with 10 cc. Et_2O, the org. solns. combined and washed with $NaHCO_3$, dried over $CaCl_2$ and distd. yielded 17.8 g. PrOAc contg. 32% iso-PrOAc. PrN(NO)Ac (27 g.) in 200 cc. AcOH decompd. by heating at 70° yielded 6.1 g. PrOAc contg. 40% iso-PrOAc. II at 0°/200 mm. passed into 35 cc. AcOH and 2 cc. Ac_2O produced 2.3 g. esters contg. 33% iso-PrOAc. These reactions apparently all take place by formation of PrNN ion and its consequent decompn. The effects of solvation and of orientation on the alkyl diazonium ion-pairs and the consequent restriction of alkyl isomerization are discussed. $MeC_6H_4SO_2Pr$ (cf. Gilman and Beaber, C.A. 19, 977) in 150 cc. pure AcOH refluxed 13 days at 120°, the PrOAc distd. with AcOH, and after diln. with H_2O azeotropically distd. yielded 8.2 g. PrOAc contg. 2.5-3% iso-PrOAc. II in Et_2O at 0° **stirred** with dropwise addn. of dry Cl_3CCO_2H in Et_2O, the washed and dried mixt. evapd., and the product distd. gave Cl_3CCO_2Pr, b12 64-9°, contg. 1.1 ± 0.3% iso-PrO_2CCCl_3. In the decompn. of Ph_2CHCHN_2 (III) in nonpolar solvents the Ph shift predominates. Ph_2CHCN (30 g.) in 250 cc. Et_2O added dropwise in 1 hr. to 0.18 mole $LiAlH_4$ in 380 cc. abs. Et_2O, the mixt. refluxed 4 hrs. and treated cautiously with 6 cc. H_2O, 4.5 cc. 20% NaOH, and 20 cc. H_2O, filtered and the residue digested with 100 cc. Et_2O, the combined Et_2O solns. dried and satd. with dry HCl, the pptd. chloride (27.0 g.) converted to the free amine, and crystd. from Ac_2O gave prismatic Ph_2CHCH_2NHAc, m. 89°, transformed to $Ph_2CHCH_2N(NO)Ac$ (IV), m. 42-4°, converted by stirring in abs. EtOH at -10° with NaOEt to Ph_2CHCHN_2 (V). IV (5.5 g.) in 90 cc. xylene slowly heated at 120-5° liberated 18.5 millimoles N and evapd. in vacuo gave 0.68 g. PhCH:CHPh (VI), m. 123.5-4.5° (from EtOH), and 3.35 g. α,β-diphenylethyl acetate (VII). Sapon. of VI with 1.6 g. KOH in 35 cc. boiling MeOH, crystn. of the neutral portion from alc. to yield 0.10 g. VI, and addn. of H_2O to the warm alc. mother liquor gave 2.1 g. $Ph(PhCH_2)CHOH$ (VIII), m. 66° (from petr. ether). On the basis of the yield of N, the decompn. of IV yielded 23% VI and 57% VIII. The infrared analysis of the crude product from another decompn. showed yields of 14% VI and 72% VII. IV (6.0 g.) in xylene **stirred** 20 min. in 40 cc. 0.1 mole KOEt in xylene at 0°, the mixt. washed with ice H_2O, dried over KOH and filtered, the dark red soln. decompd. at 90° with 10 cc. AcOH in 40 cc. xylene with evolution of 10 millimoles N in 20 min., and the product worked up gave 12% VI and 60% VII on the basis of 10 millimoles IV. The C_6H_6 soln. of V (from IV as above) decompd. by portionwise addn. of BzOH in C_6H_6 at 20° and the cryst. crude product (4.3 g.) fractionally crystd. from EtOH and MeOH yielded

0.18 g. VI and 1.50 g. α,β-diphenylethyl benzoate, m. 69-71°. Ph(p-MeOC6H4)CHCN reduced with LiAlH4 gave 68% amine HCl salt, m. 182-4°, converted by Ac2O to Ph(p-MeOC6H4)CHCH2NHAc, m. 111°, and nitrosated to the nitroso compd. (IX), was dried over **P2O5** to give 97% pure material. IX (8.0 g.) heated 2 hrs. at 105-10° in 200 cc. tech. pseudocumene with evolution of 24 millimoles N, the solvent evapd. at 12 mm., the residue (7.0 g.) taken up in MeOH, and refrigerated gave 0.60 g. p-MeOC6H4CH:CHPh; the mother liquor evapd., and the red oily residue in C6H12 chromatographed over Al2O3 gave 6.1 g. orange mixt. of esters contg. 3.14 g. p-MeOC6H4CH2CHPhOAc (X) and 2.47 g. p-MeOC6H4CH(CH2Ph)OAc (XI) (by infrared analysis). The decompn. of IX yielded 45% X, 35% XI, and 11% p-MeOC6H4CH:CHPh. This relative shift of p-MeOC6H4 and Ph in the ratio 13:10 leads to the conclusion that an energy-rich carbonium ion and not a phenonium ion (cf. Winstein, et al., C.A. 48, 2647f) is intermediate in the decompn.

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GI For diagram(s), see printed CA Issue.

AB OXAZOLE SECTION: New methods for constructing the oxazole ring have been devised and the behavior of functional groups elucidated. The synthesis of oxazoles and imidazoles from K β-hydroxy-α-(α-alkoxyalkylideneamino)acrylates is given. A mixt. of 51.1 g. AmCN and 24.5 g. EtOH was kept with 19.2 g. dry HCl below 0° for 2 wk, decompd. with 74 g. K2 CO3 in Et2O and distd. The crude AmC(OEt):NH (62.4 g.), b11 52-65°, was shaken with cold aq. H2NCH2CO2Et.HCl for 1 h. The upper layer was fractionated to yield Et α-ethoxycaprylideneaminoacetate (I),b0.5 91°, sapond. on gentle warming to AmCO2Et. The corresponding Me α-methoxycaprylideneaminoacetate (Ia), b0.1 74°, was similarly prepd. A soln. of 0.85 g. K in 2.5 g. EtOH and 14 g. Et2O was dild. to 50 mL. with Et2O, cooled to -15° and treated with a similarly cooled mixt. of 4.85 g. I and 3.2 g. HCO2Et, yielding after 3 h. at -10°, 2.6 g. of hygroscopic needles of C5H11C(OEt):NC(CO2Et):CHOK (II). The corresponding K Me β-hydroxy-α(α-methoxycaprylideneamino) acrylate (IIa) was obtained in 3.2 g.-yield from 3.75 g. Ia. Treatment of 2.6 g. II and 1.25 g. DL-penicillamine in 5 cc. EtOH with alc.-HCl gave cryst. DL-N-caproylpenicillamine, m. 137-8°. Treatment of II with ethereal HCl produced Et 2-amyloxazole-4-carboxylate, b0.07 99° (dinitrophenyl-hydrazone, m. 165-6°; amide,

m. 152°) sapond. to 2-amyloxazole-4-carboxylic acid, m. 92-3° (PhNH2 salt. m.98.5-9.5°) readily decarboxylated to 2-amyloxazole, b. 172-3°; picrate, m. 84.5-5.5°. This general synthesis of 2-substituted oxazoles and their 4-carboxylic acids has been extended to Et 2-phenyloxazole-4-carboxylate, m. 69-70°, the corresponding acid, m. 209°, and carried through to the known 2-phenyloxazole. The method can be also applied to the synthesis of imidazoles. Treatment of I with aq. NH4OH gave 2-amylimidazole-4-carboxylic acid, m. 230° (decompn.); with MeNH2.HCl or alc. H2NCH2CO2Et.HCl, I produced, resp., Et 2-amyl-1-methylimidazole-4-carboxylate (III), m. 42-3°, and Et 2-amylimidazole-4-carboxylate-1-acetate (IIIa), m. 61°. Similarly, Ia gave Me 2-amyl-1-methylimidazole, m. 66.7°, and Me 2-amylimidazole-4-carboxylate-1-acetate, m. 107°. Hydrolysis of III and IIIa yielded 1-methyl-2-amylimidazole-4-carboxylic acid, m. 121-3°, and 2-amyl-4-carboxyimidazole-1-acetic acid, m. 132-4°. Starting from PhCH2CN, Et 2-benzylimidazole-4-carboxylate-1-acetate, m. 111-2°, was likewise prepd., converted by treating with MeOH into a Me Et ester. On heating with aq. NH4OH and with PhNH2, 2-amyloxazole-4-carboxylic acid was converted into 2-amylimidazole, m. 33-4° and 1-phenyl-2-amylimidazole, m. 143-4°. Synthesis of oxazoles by rearrangement of oxazolones. The Na salt of 2-benzyl-4-hydroxymethylene-5-oxazolone (2.7 g.) in 50 mL. abs. MeOH was treated with 5 mL. abs. Et2O contg. 0.38 g. HCl. The gummy product (2.28 g.) was taken up in 10 mL. abs. MeOH and heated for 30 min. with 6.2 mL. H2O contg. 0.42 g. NaOH. The residue on evapn. was dissolved in 10 mL. of iced H2O, acidified with dil. HCl to pH 6.5 and extd. with Et2O, yielding 700 mg. 2-benzyloxazole-4-carboxylic acid, m. 158°. On heating at 220°, crude 2-phenyl-4-(α-hydroxyethylidene)-5-oxazolone rearranged to 2-phenyl-5-methyloxazole (IV), m. 184-5° (decompn.). Similarly, on heating to 230°, Na 4-hydroxymethylene-g-amyl-5-oxazolone rearranged to 2-amyloxazole-4-carboxylic acid. Evapn. of 2-(1-pentenyl)-4-(hydroxymethylene)-5-oxazolone in NaOH and fusion of the residue at 250° under reduced pressure yielded 2-pentenyl-oxazole-4-carboxylic acid, m. 145-7°. Incidental syntheses of oxazole derivs. The action of PhSO3Ag on Me thiobenzylpenaldate di-Et acetal produced colorless prisms of 2-benzyloxazole-4-carboxylic acid, m. 156-7° and the dehydration of Et α-benzylamino-acetoacetate gave Et 2-phenyl-5-methyloxazole-4-carboxylate, m. 51-2°, hydrolyzed to the acid, m. 180-1°, decarboxylated at 220° in the presence of a trace of CuO to IV. Thus a reaction known to succeed with α-acylamino ketones and carboxylic esters is extended to β-keto esters. The 2-substituted oxazoles and their 4-carboxylic acids and esters are feebly basic, readily oxidized by

cold aq. $KMnO_4$ but stable to Br in CCl_4. The ring opens on warming with 2,4-$(O_2N)_2$-$C_6H_3NHNH_2$ in 2N HCl with a tendency to formation of glyoxal osazone derivs. Rosenmund redn. of 2-amyloxazole-4-carboxylic acid chloride produced 2-amyloxazole-4-carboxaldehyde, b8 108° (2,4-dinitrophenylhydrazone, m. 172-3°), converted by warming with D-penicillamine-HCl in AcOH to the thiazolidine, devoid of antibiotic properties. From the corresponding Et ester, 2-benzyl-4-carboxyoxazole hydrazide, m. 81-3° and benzylamide, m. 121-2° were prepd. In attempts to synthesize the thiazolidine-oxazolone structure for penicillin, attention was directed to the prepn. of 5-alkoxyoxazoles and many variations of the general method of dehydrating α-acylamino esters with **P_2O_5** were introduced. By the use of PCl_5, **P_2O_5**, $POCl_3$, $SOCl_2$, and $PhSO_2Cl$, the following new oxazoles were prepd. (substituent given): 2-Ph, 5-MeO, b9 141°; 2-Ph, 5-$PhCH_2O$, m. 56°; 2-$PhCH_2$, 5-EtO, b15 152-4°; 2-$PhCH_2$, 5-MeO, m.31-2°; 2-Am, 5-EtO, b0.8 82-5°; 2-Am, 5-MeO, b1.0 60-65°; 2-(1-C_5H_9), 5-EtO, b20 125-8° (C_5H_9 = pentenyl); 2-(1-C_5H_9), 5-MeO, b15 108-10°; 2-PhCH:CH, 5-EtO, m. 35°; 2-PhCH:CH, 5-Ph CH_2O, picrate, m. 135° (decompn.); 2-Ph, 4-Me, 5-EtO, b10 151°; 2-Ph, 4-Me, 5-$PhCH_2O$, picrate, m. 112-13°; 2-$PhCH_2$, 4-Me, 5-EtO, b15 145-50°; 2-Am, 4-Me, 5-EtO, b3 92°; 2,4-Ph_2, 5-EtO, m. 47-8°; 2-Ph, 4-$PhCH_2$, 5-EtO, picrate, m. 105°; 2-Ph, 4-$PhCH_2$, 5-$PhCH_2O$, picrate, m. 117°; 2,4-$(PhCH_2)_2$, 5-EtO, b0.3 145-50°; 2-Am, 4-PhCH:CH, 5-EtO, m. 92°; 2-Ph, 4-CO_2Et, 5-EtO, m. 75°; 2-Am, 4-CO_2Et, 5-EtO, b0.1 122-5°; 2-(1-C_5H_9), 4-CO_2Et, 5-EtO, b0.2 125°; 2-$PhCH_2$, 4-CO_2Et, 5-EtO, b0.1 165°. The possibility of converting an alkoxyoxazole to the corresponding oxazolone was realized by the catalytic hydrogenation of 2 g. of 2-phenyl-5-benzyloxyoxazole in 30 mL. dry dioxane in the presence of Pd-black to 2-phenyl-5-oxazolone, m. 91°. The converse reaction, transformation of an oxazolone to an alkoxyoxazole, has also been achieved. Methylation of 3 g. of 2-phenyl-4-carbethoxy-5-oxazolone with 500 mg. CH_2N_2 in 50 mL. Et_2O yielded 2-phenyl-4-carbethoxy-5-methoxyoxazole, m. 72°. Similarly, methylation of 2-phenyl-4-carbomethoxy-2-oxazolin-5-one gave 2-phenyl-4-carbomethoxy-5-methoxyoxazole, m. 98°, identical with that prepd. by the dehydration of $BzNHCH(CO_2Me)_2$ with PCl_5 in CCl_4. Attempts to obtain 5-alkoxyoxazole-4-carboxaldehydes covered a wide range. Formylation of $BzNHCH_2CO_2Et$ and condensation with $PhCH_2NH_2$ in Et_2O gave Et β-benzylamino-α-benzamidoacrylate, R'NHCH:C(CO_2Et)NHCOR (V; R = Ph, R' = $PhCH_2$), m. 108°, cyclized by PBr_3, $POCl_3$ or PCl_5 to 2-phenyl-4-benzylaminomethylene-5-oxazolone (VI), m. 134-7; Ac deriv., m. 140°. In the same way, Et β-benzylamino-α-phenylacetamido acrylate (VIa) with PBr_3 gave 2-benzyl-4-

benzylaminomethylene-5-oxazolone (VIb). Dehydration of Et α-benzamido-β,β-diethoxypropionate with PCl_5-$POCl_3$ yielded 2-phenyl-4-(ethoxymethylene)5-oxazolone (VII). Distn. of benzyl α-benzamido-β,β-diethoxypropionate gave a mixt. of products including benzyl α-benzamido-β-ethoxyacrylate, m. 108-10°; benzyl 2-phenyloxazole-4-carboxylate, m. 106-7°; and VII. Attempts were made to cyclize α-benzyl-β-methyl-DL-phenylpenicilloate, HN.CH(CO2R').CMe2.S.CHCH(NHCOR)CO2CH2Ph (VIII, R = Ph, R' = Me) (VIIIa), m. 130°; dibenzyl-DL-phenylpenicilloate (VIII, R = Ph, R' = PhCH2) (VIIIb), m. 107-8°; and DL-2-(carboxy-1-hexenoylaminomethyl)-5,5-dimethyl-4-carbometh-oxythiazolidine benzyl ester (VIII, R = 1-pentenyl, R' = Me). (VIIIc). The action of PCl5 on VIII and VIIta gave definite evidence of formation of thiazolidinylalkoxyoxazoles and cyclization of VIIIb and chromatog. purifn. of the product gave benzyl 2-(2-phenyl-5-benzyloxy-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylate, m. 120-5°, absorption band at 2850 A. This reduced in EtOAc using a Pd-BaSO4 catalyst with 2 mol H, corresponding to removal of 2 PhCH2 groups, yielded a product with no-antibiotic activity. The simpler thiazolidines were also investigated. The reaction of 3-methyl-2-(benzamidocarbethoxymethyl)-thiazolidine with PCl5 gave a Cl-contg. product, converted by NaHCO3 to a probable sulfoxide. With PCl3, a product was obtained, which was converted by aq. KOH to 2-phenyl-4-hydroxymethylene-5-oxazolone. β-Methylaminoethyl mercaptan-HI (from 15 g. of-2-methylthiazoline-MeI) in 20 mL. H2O was treated with 11 g. of crude Na salt of C,N-diformylglycine Et ester and neutralized with AcOH. After 15 h., NaHCO3 was added and the dried CHCl3 exts. (120 mL.) were concd. to give 6.55 g. of crude product, converted by treatment with 65.5 mL. of 10% HCl in EtOH to 4.4 g. of 2-(aminocarbethoxymethyl)-3-methylthiazolidine-2HCl (IX), m. 169-70° (decompn.). IX (10.0 g.) in 36.1 mL. of 2N NaOH and 35 mL. EtOH was **stirred** with 6.6 g. PhCH2CS2Me for 45 h., yielding 6.2 g. of colorless prisms of 2-[(phenylthioacetamido)carbethoxymethyl]-3-methylthiazolidine (X), m. 100-100.5°. Addn. of 5.0 g X in 20 mL. CHCl3 to8.6 g. PhSO3Ag and 2.5 mL. pyridine in 70-mL. CHCl3 gave no identifiable org. products. The action of PhSO3Ag on Me α-phenylthioacetamido-β,β-diethoxypropionate yielded a product from which Me-benzylpenaldate and 2-benzyloxazole-4-carboxylic acid were isolated. By the PCl5 method it has been possible to prep. 4-(2-thiazolyl)-2-benzyl-5-ethoxyoxazole and 2-(p-nitrophenyl)-4-(5,5-dimethyl-4-carbomethoxy-2-thiazolinyl)-5-ethoxyoxazole. Attempts to introduce a CHO group into the 4-position of 2-phenyl-5-ethoxyoxazole (XI) using PhNMeCHO and POCl3 gave 2-phenyl-4-anilinomethylene-5-oxazoline. With AcNHBr, XI gave 2-phenyl-4-bromo-5-ethoxyoxazole, b0.8 128°. The oxidn. of 2-phenyl-4-methyl-5-ethoxyoxazole with SeO2, CrO3 or CrO2Cl2

resulted only in far-reaching breakdown. Condensation of PhCH2CH2COCO2H with AcNH2 or AmCONH2 gave α-acetamido- and α-caproyl-amino-γ-phenylisocrotonic acid (XII). Treatment of the Et ester of XII with PCl5 afforded 2-amyl-4-styryl-5-ethoxyoxazole (XIII), disrupted by ozonization with prodn. of BzOH and H2NCOCO2Et. XIII (5.7 g.) in 100 mL. glacial AcOH was **stirred** with 9.0 g. of Pb(OAc)4 for 3 h., yielding 6.1 g. of 2-(1-acetoxyamyl)-4-styryl-5-ethoxyoxazole, m. 90-1°, degraded by distn. with loss of AcOH to 2-(1-pentenyl)-4-styryl-5-ethoxyoxazole (XIV), m. 100°, reduced catalytically to XIII. Oxidn. of 2.83 g. XIV in 30 mL. tert-BuOH contg. 0.75 g. H2O2 and 30 mg. OsO4 at 40-50° for 2 h. produced PrCHO and 5-ethoxy-4-styryloxazole-2-carboxaldehyde, m.130.5°, converted into the thiazolidine, m. 169°, using DL-penicillamine. Cyclization of AmCONHCH(CO2Et)2 in dry alc. free CHCl3 with PCl5, yielded 2-amyl-5-ethoxyoxazole-4-carboxylic acid (XIV), m. 63.4°, which on refluxing with PCl5 in CHCl3 gave Et 2-amyl-5-chlorooxazole-4-carboxylate (XV), b0.3 106°, catalytically reduced over Pd-BaSO4 in xylene to 2-amyloxazole-4-carboxylate, acidified to the free acid (XVa), m. 93-4°, converted by alc. EtONa to XIV. Treatment of 2 g. XVa with 1.09 g. PCl5 in 10 mL. CHCl3 and distn. produced the corresponding acid chloride, b0.3 96°, converted by (NH4)2CO3 in aq. NH4OH to the amide, m. 90°, which, distd. with **P2O5**, gave 2-amyl-5-chloro-4-cyanooxazole (XVb), b0.15 72°. Redn. of 3.0 g. XVb in a suspension of 5.7 g. anhyd. SnCl2 in 40 mL. dry ether yielded unstable 2-amyl-5-chloro-oxazole-4-carboxaldehyde (XVI) (dinitrophenylhydrazone, m. 109-10°), rearranging in 3 days at room temp. or on low pressure distn. to 2-amyloxazole-4-carboxylic acid chloride. Despite its instability, XVI readily combined with D-penicillamine-HCl to produce D-2-(2-amyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylic acid-HCl, m. 150-2° (decompn.). A similar series of compds. starting with Et 2-phenyl-5-ethoxyoxazole-4-carboxylate (XVII) and proceeding to the thiazolidine was later prepd. XVII was sapond. to the cryst. acid (XVIIa), m. 148°, converted to the acid chloride (XVIIb), m. 105-6°, and to Et 2-phenyl-5-chlorooxazole-4-carboxylate, m. 68°, by refluxing in xylene for 1 h. The corresponding acid (XVIII), m. 178-4° (decompn.), was converted through the acid chloride, m. 118-20°, the amide, m. 183°, and the cyano compd., m. 112°, to 2-phenyl-5-chlorooxazole-4-carboxaldehyde (XIX), m. 91-3°. The addn. of 1.14 g. aldehyde in 5 mL. EtOH and 10 mL. Et2O to 0.93 g. D-penicillamine-HCl in 5 mL. H2O and 0.65 g. AcONa, and passage of HCl through a filtered ethereal soln. of the reaction product, yielded 1.5 g. of 2-(2-phenyl-5-chloro-4-oxazolyl)-5,5-di- methylthiazolidine-4-carboxylic acid-HCl, m. 178° (decompn.); Me ester-HCl, m. 120-2°; free acid, m.

166°; Me ester, m. 154°; PhCH2 ester, m.
116-7°. The thiazolidine exhibited a low order of antibiotic activity. A similar series of 2-benzyloxazole derivs. have been prepd. but the corresponding thiazolidine was inactive: 2-benzyl-5-ethoxy-oxazole-4-carboxylic acid, m. 118° (decompn.); Et ester, b0.1 165°; acid chloride, m. 81-2°; 2-benzyl-5-chlorooxazole-4-carboxylic acid, m. 183° (decompn.); Et ester, b0.02 170-5°; acid chloride, m. 156-7°; cyano compd., m. 49-50°; aldehyde [dinitrophenylhydrazone, m. 173°; semicarbazone, m. 185° (decompn.)]; 2-(2-benzyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carbo-xylic acid-HCl, m. 176-7° (decompn.). By refluxing 223 mg. XVIII in 3 mL. EtOH with 40 mg. Na, the Cl was replaced by the EtO group with formation of the corresponding acid, XVIIa. Distn. of the aldehyde XIX at 0.1 mm. gave 2-phenyloxazole-4-carboxylic acid chloride, m. 107-8°, transformed by stirring with cold concd. aq. NH4OH to the amide. Similarly the acid chloride XVIIb was converted to the amide, m. 118-19°, rearranged by heating for a few rain. at 140° to Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 183deg;. All oxazoles found to undergo rearrangement may be formulated as 5-substituted oxazoles having a CO group in the 4-position, the general case being N:CR'.O.CR3:CCOR2 → N:CR'.O.CR2:CCOR3. Known examples of rearrangement are tabulated. Since the mol. is unstable when R3 and R2 are Et and Cl, resp., or when R3 and R2 are Cl and H, resp., it is deduced that the ethoxy aldehydes should show too great stability for successful synthesis. Cyclization of AmCONHCHCNCO2Et with **P2O5** in CHCl3 gave 2-amyl-4-cyano-5-ethoxyoxazole, b0.03 98°, not reduced to the aldehyde by SnCl2 in Et2O. No 4-acetyloxazole was obtained from the MeMgI reaction product but the isolation of Et α-caproylaminoacetoacetate (dinitrophenylhydrazone, m. 166-7°) indicated oxazole ring cleavage. The dehydration of 2-phenyl-5-ethoxyoxazole-4-carboxyamide with POCl3 or the ethylation with MeCHN2 of the crude oxazolone obtained by treating BzNHCHCNCO2H with Ac2O produced 2-phenyl-4-cyano-5-ethoxyoxazole, m. 77°. The previously unknown 5-aminooxazoles were prepd. thus: treatment of 7 g. BzNHCH(CN)CO2Et, m. 138°, in 125 mL. CHCl3 with 6.2 g. PCl5 gave 4.5 g. Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 185°, also prepd. by the action of POCl3 on Bz-NHCH(CONH2)CO2Et. Condensation of 1.18 g. H2NCH-(CO2Et)2 with 1.13 g. PhNHOEt by heating for 30 min. at 110° gave the alternative compd., formulated as 2-phenyl-4-carbethoxy-5-imidazolone, m. 275°. Similarly were prepd. Et 2-benzyl-5-aminooxazole-4-carboxylate (XX), m. 124° and the corresponding 2-benzyl-4-carbethoxy-5-imidazolone, m. 254° (decompn.); 2-(1-pentenyl)-4-carbethoxy-5-aminooxazole, m. 105°; 2-amyl-4-carbethoxy-5-aminooxazole (XXa), m.

104° and the corresponding 2-amyl-4-carbethoxy-5-imidazolone., m. 230° (decompn.). On heating at 170° for 5 min., XXa was entirely converted into AmCONHCH(CN.)CO2Et, m. 83°. Heating either XX or PhCH2CONHCH(CN)CO2Et at 160-70° for 15 min. produced an equil. mixt. with the open chain ester predominating. This same mixt. was formed by heating 2-benzyl-5-ethoxyoxazole-5-carboxylic amide, probably through initial rearrangement to the aminooxazole. Stirring 35 g. NCCH2CO2CH2Ph in 40 mL. of chilled glacial AcOH with satd. aq. NaNO2 (16.5 g.) yielded 29 g. NCC(NOH)CO2CH2Ph, m. 119°, reduced with Al-Hg to NCC(NH2)CO2CH2Ph, m. 95°, and benzoylated to NCCH(NHBz)CO2CH2Ph, m. 130°, converted by heating at 160° for 5 min. to 2-phenyl-4-carbobenzyloxy-5-aminooxazole, m. 203°. The 4-carbethoxy-5-aminooxazoles are feebly basic substances whose HCl salts dissoc. readily. XXa.HCl, on boiling with ethereal EtOH gave AmCONHCH(CONH2)CO2Et, m. 150-1°, along with NH4Cl. Treatment of 1 g. XXa in 10 mL. dry Et2O at -15° with NOCl gave a low yield of Et 2-amyloxazole-4-carboxylate, m. 92-3°. Formylation of 15 g. BzNHCH2CN in 200 mL. HCO2Et and 100 mL. benzene by addn. of NaOEt (from 2.16 g. Na) in 100 mL. benzene produced, after treatment of the intermediate BzNHC(:CHONa)CO2H with dil. H2SO4 to pH 4, 2-phenyl-5-aminooxazole-4-carboxaldehyde (XXI), m. 172-3°, probably in the tautomeric form. Formylation of AmCONHCH2CN and distn. of the product yielded 2-amyloxazole-4-carboxylic acid amide, m. 154-5°, evidently by rearrangement of XXI. The action of POCl3 on Bz-NHCH(CONH2)2 and AmCONHCH(CONH2)2, m. 231°, gave 2-phenyl-5-amino-4-cyanooxazole, m. 233° (Ac deriv., m. 202-3°), and 2-amyl-5-amino-4-cyanooxazole, m. 117°. These aminooxazoles could not be reduced to aldehydes.

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<------User Break------>

=> d l36 30-32 cbib abs hitind
COMMAND INTERRUPTED
REENTER FILE 'HCA'
AND TRY AGAIN, OR ENTER '?' FOR MORE INFORMATION.
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Your command did not complete due to a temporary system problem. To recover, reenter the file you are in now. Then, any command that is normally available to you may be used. No cost summary for the current file will be displayed. After reentering the current file you may retry your command. Also, you may wish to SAVE your search query. This can be done in any file. If you cannot access your current file, or if your command fails a second time, notify the Help Desk. Enter "HELP STN" for information on contacting the nearest STN Help Desk by telephone or by using the SEND command in STNMAIL file.

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=> file hca
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FILE COVERS 1907 - 5 Aug 2004 VOL 141 ISS 7
FILE LAST UPDATED: 5 Aug 2004 (20040805/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> d l36 30-32 cbib abs hitind

L36 ANSWER 30 OF 32 HCA COPYRIGHT 2004 ACS on STN
49:15976 Original Reference No. 49:3137a-i,3138a-i,3139a-i,3140a-i,3141a-i,3142a-i,3143a-i,3144a-i,3145a-i,3146a-i,3147a-i,3148a-i,3149a-i,3150a-i,3151a-b Oxazoles and oxazolones. Cornforth, J. W.; Clarke, H. T.; et al. (Oxford Univ.;Princeton Univ. Press). Chemistry of Penicillin 688-848 (Unavailable) 1949.

GI For diagram(s), see printed CA Issue.

AB OXAZOLE SECTION: New methods for constructing the oxazole ring have been devised and the behavior of functional groups elucidated. The synthesis of oxazoles and imidazoles from K β-hydroxy-α-(α-alkoxyalkylideneamino)acrylates is given. A mixt. of 51.1 g. AmCN and 24.5 g. EtOH was kept with 19.2 g. dry HCl below 0° for 2 wk, decompd. with 74 g. K2 CO3 in Et2O and distd. The crude AmC(OEt):NH (62.4 g.), b11 52-65°, was shaken with cold aq. H2NCH2CO2Et.HCl for 1 h. The upper layer was fractionated to yield Et α-ethoxycaprylideneaminoacetate (I),b0.5 91°, sapond. on gentle warming to AmCO2Et. The corresponding Me α-methoxycaprylideneaminoacetate (Ia), b0.1 74°, was similarly prepd. A soln. of 0.85 g. K in 2.5 g. EtOH and 14 g. Et2O was dild. to 50 mL. with Et2O, cooled to -15° and treated with a similarly cooled mixt. of 4.85 g. I and 3.2 g. HCO2Et, yielding after 3 h. at -10°, 2.6 g. of hygroscopic needles of C5H11C(OEt):NC(CO2Et):CHOK (II). The corresponding K Me

β-hydroxy-α(α-methoxycaprylideneamino) acrylate (IIa) was obtained in 3.2 g.-yield from 3.75 g. Ia. Treatment of 2.6 g. II and 1.25 g. DL-penicillamine in 5 cc. EtOH with alc.-HCl gave cryst. DL-N-caproylpenicillamine, m. 137-8°. Treatment of II with ethereal HCl produced Et 2-amyloxazole-4-carboxylate, b0.07 99° (dinitrophenyl-hydrazone, m. 165-6°; amide, m. 152°) sapond. to 2-amyloxazole-4-carboxylic acid, m. 92-3° (PhNH2 salt. m.98.5-9.5°) readily decarboxylated to 2-amyloxazole, b. 172-3°; picrate, m. 84.5-5.5°. This general synthesis of 2-substituted oxazoles and their 4-carboxylic acids has been extended to Et 2-phenyloxazole-4-carboxylate, m. 69-70°, the corresponding acid, m. 209°, and carried through to the known 2-phenyloxazole. The method can be also applied to the synthesis of imidazoles. Treatment of I with aq. NH4OH gave 2-amylimidazole-4-carboxylic acid, m. 230° (decompn.); with MeNH2.HCl or alc. H2NCH2CO2Et.HCl, I produced, resp., Et 2-amyl-1-methylimidazole-4-carboxylate (III), m. 42-3°, and Et 2-amylimidazole-4-carboxylate-1-acetate (IIIa), m. 61°. Similarly, Ia gave Me 2-amyl-1-methylimidazole, m. 66.7°, and Me 2-amylimidazole-4-carboxylate-1-acetate, m. 107°. Hydrolysis of III and IIIa yielded 1-methyl-2-amylimidazole-4-carboxylic acid, m. 121-3°, and 2-amyl-4-carboxyimidazole-1-acetic acid, m. 132-4°. Starting from PhCH2CN, Et 2-benzylimidazole-4-carboxylate-1-acetate, m. 111-2°, was likewise prepd., converted by treating with MeOH into a Me Et ester. On heating with aq. NH4OH and with PhNH2, 2-amyloxazole-4-carboxylic acid was converted into 2-amylimidazole, m. 33-4° and 1-phenyl-2-amylimidazole, m. 143-4°. Synthesis of oxazoles by rearrangement of oxazolones. The Na salt of 2-benzyl-4-hydroxymethylene-5-oxazolone (2.7 g.) in 50 mL. abs. MeOH was treated with 5 mL. abs. Et2O contg. 0.38 g. HCl. The gummy product (2.28 g.) was taken up in 10 mL. abs. MeOH and heated for 30 min. with 6.2 mL. H2O contg. 0.42 g. NaOH. The residue on evapn. was dissolved in 10 mL. of iced H2O, acidified with dil. HCl to pH 6.5 and extd. with Et2O, yielding 700 mg. 2-benzyloxazole-4-carboxylic acid, m. 158°. On heating at 220°, crude 2-phenyl-4-(α-hydroxyethylidene)-5-oxazolone rearranged to 2-phenyl-5-methyloxazole (IV), m. 184-5° (decompn.). Similarly, on heating to 230°, Na 4-hydroxymethylene-g-amyl-5-oxazolone rearranged to 2-amyloxazole-4-carboxylic acid. Evapn. of 2-(1-pentenyl)-4-(hydroxymethylene)-5-oxazolone in NaOH and fusion of the residue at 250° under reduced pressure yielded 2-pentenyl-oxazole-4-carboxylic acid, m. 145-7°. Incidental syntheses of oxazole derivs. The action of PhSO3Ag on Me thiobenzylpenaldate di-Et acetal produced colorless prisms of 2-benzyloxazole-4-carboxylic acid, m. 156-7° and the dehydration of Et α-benzylamino-acetoacetate gave Et

2-phenyl-5-methyloxazole-4-carboxylate, m. 51-2°, hydrolyzed to the acid, m. 180-1°, decarboxylated at 220° in the presence of a trace of CuO to IV. Thus a reaction known to succeed with α-acylamino ketones and carboxylic esters is extended to β-keto esters. The 2-substituted oxazoles and their 4-carboxylic acids and esters are feebly basic, readily oxidized by cold aq. KMnO4 but stable to Br in CCl4. The ring opens on warming with 2,4-(O2N)2-C6H3NHNH2 in 2N HCl with a tendency to formation of glyoxal osazone derivs. Rosenmund redn. of 2-amyloxazole-4-carboxylic acid chloride produced 2-amyloxazole-4-carboxaldehyde, b8 108° (2,4-dinitrophenylhydrazone, m. 172-3°), converted by warming with D-penicillamine-HCl in AcOH to the thiazolidine, devoid of antibiotic properties. From the corresponding Et ester, 2-benzyl-4-carboxyoxazole hydrazide, m. 81-3° and benzylamide, m. 121-2° were prepd. In attempts to synthesize the thiazolidine-oxazolone structure for penicillin, attention was directed to the prepn. of 5-alkoxyoxazoles and many variations of the general method of dehydrating α-acylamino esters with **P2O5** were introduced. By the use of PCl5, **P2O5**, POCl3, SOCl2, and PhSO2Cl, the following new oxazoles were prepd. (substituent given): 2-Ph, 5-MeO, b9 141°; 2-Ph, 5-PhCH2O, m. 56°; 2-PhCH2, 5-EtO, b15 152-4°; 2-PhCH2, 5-MeO, m.31-2°; 2-Am, 5-EtO, b0.8 82-5°; 2-Am, 5-MeO, b1.0 60-65°; 2-(1-C5H9), 5-EtO, b20 125-8° (C5H9 = pentenyl); 2-(1-C5H9), 5-MeO, b15 108-10°; 2-PhCH:CH, 5-EtO, m. 35°; 2-PhCH:CH, 5-Ph CH2O, picrate, m. 135° (decompn.); 2-Ph, 4-Me, 5-EtO, b10 151°; 2-Ph, 4-Me, 5-PhCH2O, picrate, m. 112-13°; 2-PhCH2, 4-Me, 5-EtO, b15 145-50°; 2-Am, 4-Me, 5-EtO, b3 92°; 2,4-Ph2, 5-EtO, m. 47-8°; 2-Ph, 4-PhCH2, 5-EtO, picrate, m. 105°; 2-Ph, 4-PhCH2, 5-PhCH2O, picrate, m. 117°; 2,4-(PhCH2)2, 5-EtO, b0.3 145-50°; 2-Am, 4-PhCH:CH, 5-EtO, m. 92°; 2-Ph, 4-CO2Et, 5-EtO, m. 75°; 2-Am, 4-CO2Et, 5-EtO, b0.1 122-5°; 2-(1-C5H9), 4-CO2Et, 5-EtO, b0.2 125°; 2-PhCH2, 4-CO2Et, 5-EtO, b0.1 165°. The possibility of converting an alkoxyoxazole to the corresponding oxazolone was realized by the catalytic hydrogenation of 2 g. of 2-phenyl-5-benzyloxyoxazole in 30 mL. dry dioxane in the presence of Pd-black to 2-phenyl-5-oxazolone, m. 91°. The converse reaction, transformation of an oxazolone to an alkoxyoxazole, has also been achieved. Methylation of 3 g. of 2-phenyl-4-carbethoxy-5-oxazolone with 500 mg. CH2N2 in 50 mL. Et2O yielded 2-phenyl-4-carbethoxy-5-methoxyoxazole, m. 72°. Similarly, methylation of 2-phenyl-4-carbomethoxy-2-oxazolin-5-one gave 2-phenyl-4-carbomethoxy-5-methoxyoxazole, m. 98°, identical with that prepd. by the dehydration of BzNHCH(CO2Me)2 with PCl5 in CCl4. Attempts to obtain 5-alkoxyoxazole-4-carboxaldehydes covered a wide range. Formylation of BzNHCH2CO2Et and condensation

with PhCH2NH2 in Et2O gave Et β-benzylamino-α-benzamidoacrylate, R'NHCH:C(CO2Et)NHCOR (V; R = Ph, R' = PhCH2), m. 108°, cyclized by PBr3, POCl3 or PCl5 to 2-phenyl-4-benzylaminomethylene-5-oxazolone (VI), m. 134-7; Ac deriv., m. 140°. In the same way, Et β-benzylamino-α-phenylacetamido acrylate (VIa) with PBr3 gave 2-benzyl-4-benzylaminomethylene-5-oxazolone (VIb). Dehydration of Et α-benzamido-β,β-diethoxypropionate with PCl5-POCl3 yielded 2-phenyl-4-(ethoxymethylene)5-oxazolone (VII). Distn. of benzyl α-benzamido-β,β-diethoxypropionate gave a mixt. of products including benzyl α-benzamido-β-ethoxyacrylate, m. 108-10°; benzyl 2-phenyloxazole-4-carboxylate, m. 106-7°; and VII. Attempts were made to cyclize α-benzyl-β-methyl-DL-phenylpenicilloate, HN.CH(CO2R').CMe2.S.CHCH(NHCOR)CO2CH2Ph (VIII, R = Ph, R' = Me) (VIIIa), m. 130°; dibenzyl-DL-phenylpenicilloate (VIII, R = Ph, R' = PhCH2) (VIIIb), m. 107-8°; and DL-2-(carboxy-1-hexenoylaminomethyl)-5,5-dimethyl-4-carbometh-oxythiazolidine benzyl ester (VIII, R = 1-pentenyl, R' = Me). (VIIIc). The action of PCl5 on VIII and VIIta gave definite evidence of formation of thiazolidinylalkoxyoxazoles and cyclization of VIIIb and chromatog. purifn. of the product gave benzyl 2-(2-phenyl-5-benzyloxy-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylate, m. 120-5°, absorption band at 2850 A. This reduced in EtOAc using a Pd-BaSO4 catalyst with 2 mol H, corresponding to removal of 2 PhCH2 groups, yielded a product with no-antibiotic activity. The simpler thiazolidines were also investigated. The reaction of 3-methyl-2-(benzamidocarbethoxymethyl)-thiazolidine with PCl5 gave a Cl-contg. product, converted by NaHCO3 to a probable sulfoxide. With PCl3, a product was obtained, which was converted by aq. KOH to 2-phenyl-4-hydroxymethylene-5-oxazolone. β-Methylaminoethyl mercaptan-HI (from 15 g. of-2-methylthiazoline-MeI) in 20 mL. H2O was treated with 11 g. of crude Na salt of C,N-diformylglycine Et ester and neutralized with AcOH. After 15 h., NaHCO3 was added and the dried CHCl3 exts. (120 mL.) were concd. to give 6.55 g. of crude product, converted by treatment with 65.5 mL. of 10% HCl in EtOH to 4.4 g. of 2-(aminocarbethoxymethyl)-3-methylthiazolidine-2HCl (IX), m. 169-70° (decompn.). IX (10.0 g.) in 36.1 mL. of 2N NaOH and 35 mL. EtOH was **stirred** with 6.6 g. PhCH2CS2Me for 45 h., yielding 6.2 g. of colorless prisms of 2-[(phenylthioacetamido)carbethoxymethyl]-3-methylthiazolidine (X), m. 100-100.5°. Addn. of 5.0 g X in 20 mL. CHCl3 to8.6 g. PhSO3Ag and 2.5 mL. pyridine in 70-mL. CHCl3 gave no identifiable org. products. The action of PhSO3Ag on Me α-phenylthioacetamido-β,β-diethoxypropionate yielded a product from which Me-benzylpenaldate and 2-benzyloxazole-4-carboxylic acid were isolated. By the PCl5 method it has been possible to prep. 4-(2-thiazolyl)-2-benzyl-5-ethoxyoxazole and

2-(p-nitrophenyl)-4-(5,5-dimethyl-4-carbomethoxy-2-thiazolinyl)-5-ethoxyoxazole. Attempts to introduce a CHO group into the 4-position of 2-phenyl-5-ethoxyoxazole (XI) using PhNMeCHO and POCl3 gave 2-phenyl-4-anilinomethylene-5-oxazoline. With AcNHBr, XI gave 2-phenyl-4-bromo-5-ethoxyoxazole, b0.8 128°. The oxidn. of 2-phenyl-4-methyl-5-ethoxyoxazole with SeO2, CrO3 or CrO2Cl2 resulted only in far-reaching breakdown. Condensation of PhCH2CH2COCO2H with AcNH2 or AmCONH2 gave α-acetamido- and α-caproyl-amino-γ-phenylisocrotonic acid (XII).
Treatment of the Et ester of XII with PCl5 afforded 2-amyl-4-styryl-5-ethoxyoxazole (XIII), disrupted by ozonization with prodn. of BzOH and H2NCOCO2Et. XIII (5.7 g.) in 100 mL. glacial AcOH was **stirred** with 9.0 g. of Pb(OAc)4 for 3 h., yielding 6.1 g. of 2-(1-acetoxyamyl)-4-styryl-5-ethoxyoxazole, m. 90-1°, degraded by distn. with loss of AcOH to 2-(1-pentenyl)-4-styryl-5-ethoxyoxazole (XIV), m. 100°, reduced catalytically to XIII. Oxidn. of 2.83 g. XIV in 30 mL. tert-BuOH contg. 0.75 g. H2O2 and 30 mg. OsO4 at 40-50° for 2 h. produced PrCHO and 5-ethoxy-4-styryloxazole-2-carboxaldehyde, m.130.5°, converted into the thiazolidine, m. 169°, using DL-penicillamine. Cyclization of AmCONHCH(CO2Et)2 in dry alc. free CHCl3 with PCl5, yielded 2-amyl-5-ethoxyoxazole-4-carboxylic acid (XIV), m. 63.4°, which on refluxing with PCl5 in CHCl3 gave Et 2-amyl-5-chlorooxazole-4-carboxylate (XV), b0.3 106°, catalytically reduced over Pd-BaSO4 in xylene to 2-amyloxazole-4-carboxylate, acidified to the free acid (XVa), m. 93-4°, converted by alc. EtONa to XIV. Treatment of 2 g. XVa with 1.09 g. PCl5 in 10 mL. CHCl3 and distn. produced the corresponding acid chloride, b0.3 96°, converted by (NH4)2CO3 in aq. NH4OH to the amide, m. 90°, which, distd. with **P2O5**, gave 2-amyl-5-chloro-4-cyanooxazole (XVb), b0.15 72°. Redn. of 3.0 g. XVb in a suspension of 5.7 g. anhyd. SnCl2 in 40 mL. dry ether yielded unstable 2-amyl-5-chloro-oxazole-4-carboxaldehyde (XVI) (dinitrophenylhydrazone, m. 109-10°), rearranging in 3 days at room temp. or on low pressure distn. to 2-amyloxazole-4-carboxylic acid chloride. Despite its instability, XVI readily combined with D-penicillamine-HCl to produce D-2-(2-amyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylic acid-HCl, m. 150-2° (decompn.). A similar series of compds. starting with Et 2-phenyl-5-ethoxyoxazole-4-carboxylate (XVII) and proceeding to the thiazolidine was later prepd. XVII was sapond. to the cryst. acid (XVIIa), m. 148°, converted to the acid chloride (XVIIb), m. 105-6°, and to Et 2-phenyl-5-chlorooxazole-4-carboxylate, m. 68°, by refluxing in xylene for 1 h. The corresponding acid (XVIII), m. 178-4° (decompn.), was converted through the acid chloride, m. 118-20°, the amide, m. 183°, and the cyano compd., m. 112°, to 2-phenyl-5-chlorooxazole-4-carboxaldehyde (XIX), m.

91-3°. The addn. of 1.14 g. aldehyde in 5 mL. EtOH and 10 mL. Et2O to 0.93 g. D-penicillamine-HCl in 5 mL. H2O and 0.65 g. AcONa, and passage of HCl through a filtered ethereal soln. of the reaction product, yielded 1.5 g. of 2-(2-phenyl-5-chloro-4-oxazolyl)-5,5-di- methylthiazolidine-4-carboxylic acid-HCl, m. 178° (decompn.); Me ester-HCl, m. 120-2°; free acid, m. 166°; Me ester, m. 154°; PhCH2 ester, m. 116-7°. The thiazolidine exhibited a low order of antibiotic activity. A similar series of 2-benzyloxazole derivs. have been prepd. but the corresponding thiazolidine was inactive: 2-benzyl-5-ethoxy-oxazole-4-carboxylic acid, m. 118° (decompn.); Et ester, b0.1 165°; acid chloride, m. 81-2°; 2-benzyl-5-chlorooxazole-4-carboxylic acid, m. 183° (decompn.); Et ester, b0.02 170-5°; acid chloride, m. 156-7°; cyano compd., m. 49-50°; aldehyde [dinitrophenylhydrazone, m. 173°; semicarbazone, m. 185° (decompn.)]; 2-(2-benzyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carbo-xylic acid-HCl, m. 176-7° (decompn.). By refluxing 223 mg. XVIII in 3 mL. EtOH with 40 mg. Na, the Cl was replaced by the EtO group with formation of the corresponding acid, XVIIa. Distn. of the aldehyde XIX at 0.1 mm. gave 2-phenyloxazole-4-carboxylic acid chloride, m. 107-8°, transformed by stirring with cold concd. aq. NH4OH to the amide. Similarly the acid chloride XVIIb was converted to the amide, m. 118-19°, rearranged by heating for a few rain. at 140° to Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 183deg;. All oxazoles found to undergo rearrangement may be formulated as 5-substituted oxazoles having a CO group in the 4-position, the general case being N:CR'.O.CR3:CCOR2 → N:CR'.O.CR2:CCOR3. Known examples of rearrangement are tabulated. Since the mol. is unstable when R3 and R2 are Et and Cl, resp., or when R3 and R2 are Cl and H, resp., it is deduced that the ethoxy aldehydes should show too great stability for successful synthesis. Cyclization of AmCONHCHCNCO2Et with **P2O5** in CHCl3 gave 2-amyl-4-cyano-5-ethoxyoxazole, b0.03 98°, not reduced to the aldehyde by SnCl2 in Et2O. No 4-acetyloxazole was obtained from the MeMgI reaction product but the isolation of Et α-caproylaminoacetoacetate (dinitrophenylhydrazone, m. 166-7°) indicated oxazole ring cleavage. The dehydration of 2-phenyl-5-ethoxyoxazole-4-carboxyamide with POCl3 or the ethylation with MeCHN2 of the crude oxazolone obtained by treating BzNHCHCNCO2H with Ac2O produced 2-phenyl-4-cyano-5-ethoxyoxazole, m. 77°. The previously unknown 5-aminooxazoles were prepd. thus: treatment of 7 g. BzNHCH(CN)CO2Et, m. 138°, in 125 mL. CHCl3 with 6.2 g. PCl5 gave 4.5 g. Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 185°, also prepd. by the action of POCl3 on Bz-NHCH(CONH2)CO2Et. Condensation of 1.18 g. H2NCH-(CO2Et)2 with 1.13 g. PhNHOEt by heating for 30 min. at 110° gave the

alternative compd., formulated as 2-phenyl-4-carbethoxy-5-imidazolone, m. 275°. Similarly were prepd. Et 2-benzyl-5-aminooxazole-4-carboxylate (XX), m. 124° and the corresponding 2-benzyl-4-carbethoxy-5-imidazolone, m. 254° (decompn.); 2-(1-pentenyl)-4-carbethoxy-5-aminooxazole, m. 105°; 2-amyl-4-carbethoxy-5-aminooxazole (XXa), m. 104° and the corresponding 2-amyl-4-carbethoxy-5-imidazolone., m. 230° (decompn.). On heating at 170° for 5 min., XXa was entirely converted into AmCONHCH(CN.)CO2Et, m. 83°. Heating either XX or PhCH2CONHCH(CN)CO2Et at 160-70° for 15 min. produced an equil. mixt. with the open chain ester predominating. This same mixt. was formed by heating 2-benzyl-5-ethoxyoxazole-5-carboxylic amide, probably through initial rearrangement to the aminooxazole. Stirring 35 g. NCCH2CO2CH2Ph in 40 mL. of chilled glacial AcOH with satd. aq. NaNO2 (16.5 g.) yielded 29 g. NCC(NOH)CO2CH2Ph, m. 119°, reduced with Al-Hg to NCC(NH2)CO2CH2Ph, m. 95°, and benzoylated to NCCH(NHBz)CO2CH2Ph, m. 130°, converted by heating at 160° for 5 min. to 2-phenyl-4-carbobenzyloxy-5-aminooxazole, m. 203°. The 4-carbethoxy-5-aminooxazoles are feebly basic substances whose HCl salts dissoc. readily. XXa.HCl, on boiling with ethereal EtOH gave AmCONHCH(CONH2)CO2Et, m. 150-1°, along with NH4Cl. Treatment of 1 g. XXa in 10 mL. dry Et2O at -15° with NOCl gave a low yield of Et 2-amyloxazole-4-carboxylate, m. 92-3°. Formylation of 15 g. BzNHCH2CN in 200 mL. HCO2Et and 100 mL. benzene by addn. of NaOEt (from 2.16 g. Na) in 100 mL. benzene produced, after treatment of the intermediate BzNHC(:CHONa)CO2H with dil. H2SO4 to pH 4, 2-phenyl-5-aminooxazole-4-carboxaldehyde (XXI), m. 172-3°, probably in the tautomeric form. Formylation of AmCONHCH2CN and distn. of the product yielded 2-amyloxazole-4-carboxylic acid amide, m. 154-5°, evidently by rearrangement of XXI. The action of POCl3 on Bz-NHCH(CONH2)2 and AmCONHCH(CONH2)2, m. 231°, gave 2-phenyl-5-amino-4-cyanooxazole, m. 233° (Ac deriv., m. 202-3°), and 2-amyl-5-amino-4-cyanooxazole, m. 117°. These aminooxazoles could not be reduced to aldehydes.

Satn. of 0.52 g. PhCH2CSNHCH(CN)CO2Et, m. 157°, treated in 5 mL. dry EtOH with dry HCl at -10° and the soln. evapd. after 12 h. at 20° in vacuo yielded 0.5 g. 2-benzyl-4-carbethoxy-5-aminothiazole, m. 180°. OXAZOLONE SECTION. Part. I. General Chem. of Oxazolones. Prepn. of 2-Oxazolin-5-ones. The reaction of Ac2O with α-acylamino acids is the most general procedure by which new oxazolones, O.CR:N.CR1R2.CO, have been prepd. (substituents given): 2-Me, 4-iso-Pr, b10 60°; 2-PhCH2, 4-Me, b0.5-1.0 122-3°; 2-PhCH2, 4-iso-Pr, b0.5 115-17°; 2,4-(PhCH2)2, oil; 2-Am, 4-PhCH2, b5 135-8°; 2-(2-pentenyl), 4-PhCH2, b1.0 155-7°; 2-PhCH2, 4,4-Me2 (I), m. 59.5°; 2-Ph, 4-iso-Bu, m. 56-7°; 2-PhCH2, 4-sec-Bu, b2.0

137-9°; 2-Ph, 4,4-C5H10, m. 71°; 2-PhCH2, 4-Me, 4-PhCH:CH, m. 56-7°; 2-Ph, 4-CO2Et, m. 147-8°; 2-Am, 4-CO2Et, oil; 2-Ph, 4-(p-MeOC6H4CH2); 2-PhCH2, 4-(p-MeOC6H4CH2); and 2-PhCH2, 4-iso-Bu. Similarly, heating 100 g. BzNHCH2CO2H (II) in 300 mL. Ac2O at 100° yielded 49 g. 2-phenyl-2-oxazolin-5-one (III), m. 94-5°, the only monosubstituted oxazolone prepd. by this method. By warming BzNHCHPhCH2CO2H in CHCl3 with 1 equiv. of 2-benzyl-4-methyl-5-oxazolone, a good yield of 2-phenyl-4-benzyl-5-oxazolone, m. 68-9°, was obtained. Addn. of 1 g. NaNO2 in 20 mL. H2O to 3 g. of BzNHC(CONHNH2):-CHPh in 30 mL. N HCl gave α-benzamidocinnamic azide, m. 113-4° (decompn.), converted on boiling with EtOH or treatment with pyridine at room temp. to 2-phenyl-4-benzylidene-5-oxazolone (IV). Similarly, Me2C:C(NHBz)-CON3 was converted to 2-phenyl-4-isopropylidene-5-oxazolone (IVa). These type II (unsatd. substituent at the 4-position) unsatd. oxazolines are formed more readily than the above-listed type I (satd. substituent at the 4-position) satd. oxazolones to which the azide conversion could not be extended. Redn. of IV over Pd-C gave 2-phenyl-4-benzyl-5-oxazolone (V), m. 67-8°. IVa was similarly reduced in dioxane to give an oil which, treated with PhNH2 in benzene, produced Me2CHCH(NHBz)CONHPh, m. 211-2°. The possibility arose that any reagent capable of transforming an acid to its chloride might be expected to convert an α-acylamino acid to the corresponding oxazolone. Thus treatment of II in 15 mL. dioxane with 2 mL. PBr3 gave III. Similarly, 14.5 g. PhCH2CONHCMe2CO2H in 150 mL. dioxane was treated with 18 g. PBr3. The solid product suspended in dioxane and treated with slight excess of CH2N2 in ether yielded I, converted by PhCH2NH2 into PhCH2CONHCMe2CONH2, m. 122-3°. Treatment of PhCH2CHNHBzCO2H in pyridine with PBr3 likewise gave the known V. Attempts to prep. 2-benzyl-5-oxazolone from PhCH2CONHCH2CO2H gave an unstable oil, converted by PhCH2NH2 into PhCH2CONHCH2CONHCH2Ph. Conversion of PhCH:C(NHBz)CO2H into IV was effected by POCl3, SOCl2, pyridine, by ClCH2COCl and K2CO3, and by AcCl in dioxane. Oxazolones have been produced by treating PhCH2OCOCl with acylamino acids. Apart from direct dehydration, three methods are known for the prepn. of type II oxazolones; the Erlenmeyer aldehydeacylglycine synthesis, the Bergmann-Stein reaction of N-(α-haloacyl)amino acids with Ac2O, and the dehydration of β-hydroxy-α-acylamino acids. In that III reacts with Me2CO in the presence of NaOAc to yield IVa in the absence of Ac2O, it is suggested that III is an intermediate in the Erlenmeyer synthesis. In the presence of a little pyridine, BzH condenses with III to produce IV. Similarly, 2-phenyl-4-propylidene-5-oxazolone, m. 88-9°, was obtained in good yield from III and EtCHO. By adding Ac2O dropwise with stirring to 17.9 g. II and 6.1 g. fused NaOAc in 580 mL. Me2CO, refluxing for 3-4 h. at 59-62°, pouring the reaction mixt. over 200 g. ice and dilg. to 1500 mL. produced high yields (73%) of

relatively pure 2-phenyl-4-isopropylidene-5-oxazolone, m. 98°. Condensation of II with (EtO)2CHCHO and Ac2O gave 4,4'-glyoxalidenebis(2-phenyl-5-oxazolone), m. 325° (decompn.). Though no acyl interchange in the Erlenmeyer synthesis occurs with II, the formation of 2-methyl-4-benzylidene-5-oxazolone occurs when either PhCH2CONHCH2CO2H or AmCONHCH2CO2H (VI) is refluxed with BzH in the presence of Ac2O and NaOAc. Refluxing VI (15.1 g.) with 13.1 g. AmCO2Na and 61 g. (AmCO)2O in 49 mL. Me2CO for 24 h. at 75° gave α-caproyl-amino-β,β-dimethylacrylic acid, m. 162-3°, converted by melting and heating in vacuo at 180-90° into 2-amyl-4-isopropylidene-5-oxazolone, b0.03 60-2°. By Bergmann's method, 2-methyl-4-isopropylidene-5-oxazolone (VII) and 2-methyl-4-sec-butylidene-5-oxazolone were prepd. from Me2CHCH2CH(NHCOCH2Cl)CO2H and EtMeCHCH-(NHCOCH2Cl)CO2H. Carter's method was used to prep. VII by the action of Ac2O on Me2C(OMe)CHNH2CO2H. Ring opening Reactions of Oxazolones. The general **reaction** of oxazolones **with** H2O, **ROH**, RSH, NH3, RNH2 and RR'NH represented by O.CR:N.CR1R2.CO + HX → OCRHNCR1R2COX, suggested originally the thiazolidine-oxazolone formulation of penicillin. Comparison of the reactivity of V with that of IV showed the former to be rapidly hydrolyzed by 2N aq. acid or alkali under conditions not affecting the latter. V reacts with ROH more rapidly than III. In the presence of NaOMe or PhCH2NMe3-OH, IVa was converted quant. to Me2C:C(BzNH)CO2Me, m. 130-1°. The methanolysis of 2-benzyl-4-p-methoxybenzyl-5-oxazolone in dry abs. MeOH yielded (N-phenylacetyl-p-methoxyphenylalanyl)-p-methoxyphenylalanine, m. 199-200°. The formation of the dipeptide may be due to an "ortho-ester" reaction with the imino-ether form of the oxazolone. Reaction of PhCH2SH with III and I yielded benzyl hippurate, m. 101-2° and Me2CHCH(NHCOCH2Ph)COSCH2Ph, m. 138.5°. Almost all types of oxazolones react with PhCH2NH2 to form α-acylaminoacyl-benzylamides. The reaction of V with d-MePhCHNH2 in dry dioxane was followed polarimetrically and at const. rotation, produced N-benzoylphenylalanine-d-N-α-phenylethylamide, m. 178-80°, [α]D23 28.5° (c 1, dioxane). The strongly enolyzed 2-phenyl-4-carbethoxy-5-oxazolone formed a salt with PhCH2NH2, converted on heating in xylene to the benzylamide, m. 132°. The reaction of PhNH2.HCl with III and 2-benzyl-4-sec-butyl-5-oxazolone gave the normal anilide and the corresponding acid. Reaction of V and 2-phenyl-4-isobutyl-5-oxazolone with L-HSCH2CH-(NH2)CO2Me produced the normal amides, m. 128-9°, and 131-5°, resp., the NH2 group taking precedence over the SH group in the condensation. The action of N2H4 on oxazolones has been clarified. The addn. of 18 g.-phenyl-4-methyl-5-oxazolone to excess 60% N2H4.H2O in EtOH and heating to 50-60° for 30 min. gave 17.5 g. benzoylalanine

hydrazide, m. 142-4°; benzylidene deriv., m. 193-4°. Treatment of IV with N2H4.H2O also gave the normal hydrazide, PhCH:C(NHBz)CONHNH2, m. 113-14°, converted by heating the corresponding azide in xylene to 2-oxo-4-benzylidene-6-phenyl-1,3,5-oxadiazine, m. 174° (decompn.). Conversion of Me2C:C(NHBz)CON3 similarly produced 2-oxo-4-isopropylidene-6-phenyl-1,3,5-oxadiazine, m. 166-8°. A mixt. of 5 g. IV, 10 mL. N2H4.H2O and 3 mL. EtOH was refluxed for 30 min. yielding 4-benzamido-3-phenyl-5-pyrazolidone, m. 228-9°, identical with the product formed by refluxing PhCH:C(NHBz)CONHNH2 (VIII), m. 157-8°, which N2H4.H2O for 30 min. Similarly, the hydrazide Me2C:C(NHBz)CONHNH2, m. 192-4°, was converted into 3,3-dimethyl-4-benzoylamino-5-pyrazolidine, m. 106-8°. The hydrazide VIII was boiled in N NaOH and the sparingly sol. salt on acidification gave 6-hydroxy-5-benzyl-3-phenyl-1,2,4-triazine, m. 175-6°; Ac deriv., 187-8°. Oxidn. of XIII with K3Fe(CN)6 produced N,N'-bis(α-benzoylaminocinnamoyl)hydrazine, m. 265°, together with a substance, m. 186-7°, with the probable structure PhCH:C.CH(OH).NBz.C-(:CHPh).CH(OH).NBz, forming PhCH2CH(NHBz)-(CO2H) on alk. hydrolysis. REACTIONS OF TYPE II OXAZOLONES: Some reactions involving the double bond in type II oxazolones have been discovered. Treatment of IV in dry dioxane with 2 mol CH2N2 in dry Et2O at 0° and allowing the soln. to stand overnight at room temp. gave product, C17H13O2N, m. 142-3°. Addn. of liq. NH3 to IVa with shaking and cooling in solid CO2 gave a small yield of basic product, C12H17O2N3, m. 162-6°, probably by addn. of 2 mol NH3. Addn. of H2S and RSH to the double bond has been studied in connection with various syntheses of penicillamine. The addn., of 136 g. IVa in 675 mL. dry benzene to 3.38 g. Na in 675 mL. of chilled dry MeOH and 76.5 mL. PhCH2SH produced Me2CC(NHBz)CO2Me, m. 137-8°, and Me2C(SCH2Ph)CH(NHBz)CO2Me, m. 66-7°. The addn. probably takes place after ring opening, since the oxazolone can be replaced by an acrylic ester. Similarly, IV under like conditions, gave PhCH(SCH2Ph)CH-(NHBz)CO2Me, m. 164°. There is no evidence of direct addn. of PhCH2SH to the double bond. Addn. of H2S to IVa and VII in the presence of Et3N yielded Me2C(SH)CH(NHBz)COSH and Me2C(SH)CH(NHAc)COSH, resp. The initial step is probably the addn. of H2S to the double bond. Anhyd. MeOH satd. with H2S at 0° treated with IVa gave 2,5,5-trimethyl-2-thiazoline-4-carboxylic acid, b25 120°; picrate, m. 159°, probably formed by addn., followed by displacement. IV similarly yielded 2-phenyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid, m. 124-6°. IVa was apparently converted by treatment with alc. NaSH to 2-phenyl-4-isopropylidene-5-thiazolone, m. 100.5-101.5°. The reactivity of the Me groups in IVa is sufficient to permit condensation reactions with BzH to produce 2-phenyl-4-benzylideneisopropylidene-5-oxazolone, m. 135°. A

mixt. of stereoisomers, m. 134-6°, was produced by heating a mixt. of 35.8 g. BzNHCH2CO2H, 32 g. PhCH:CHAc, 15 g. of fused NaOAc and 50 mL. Ac2O for 3 h. at 100°. IVa is a pseudo-acid and exhibits weak violet fluorescence in Et3N. On addn. of NaOMe to IVa in MeOH, the initial intense blue-violet fluorescence in UV light due to the presence of the propenyloxazole soon disappears with the formation of Me2C:C(NHBz)CO2Me by ring opening. Misc. REACTIONS OF OXAZOLONES. Excess PhMgBr was added to 6.0 g. 2-phenyl-4-methyl-5-oxazolone in Et2O and after refluxing for 6 h. the reaction product was hydrolyzed and extd. with Et2O, yielding 4.6 g. 1,1-diphenyl-2-benzoylamino-propanol, m. 192-3°. With AgClO4 in benzene, III in EtOH gave a complex, m. 146° (decompn.). A similar cryst. compd., m. 172° (decompn.) was formed with 2-benzyl-4-methyl-5-oxazolone (IX). Formylation of 2,4-diphenyl-5-oxazolone apparently produced a stabilized enolic form, PhC:N.CPh:COH.O, m. 110°. Oxidn. of 2-phenyl-4-isobutyl- and 2-phenyl-4-benzyl-5-oxazolones with Hg(OAc)2 gave the corresponding 4,4'-bisoxazolones, m. 138-42°, and 201-202.5°, resp. PSEUDO-OXAZOLONES. According to the method of Bergmann, 12 g. PhCHBrCONHCH2CO2H was added to 5 mL. dry pyridine and 100 mL. Ac2O and after 2.5 h. at 0° was poured over ice. The solid product was dried over NaOH and crystd. from warm MeOH by cooling to -50°, yielding 64% of 2-benzylidenepseudooxazolone (2-benzylidene-3-oxazolin-5-one), m. 92-4°, hydrolyzed by 0.5N HCl in acetone to PhCH2-CONH2, m. 153-7°. An attempt to prep. 2-benzyl-4-methylene-5-oxazolone by Bergmann's method from Ph-CHClCONHCHMeCO2H gave the potent skin irritant 2-benzylidene-4-methylpseudo-5-oxazolone (X), m. 105-115°, hydrolyzed by aq. acetone to PhCH2CONH2 and AcCO2H, suggesting that the pseudooxazolones are intermediates in the Bermann synthesis of type II oxazolones and that, in general, the latter are in dynamic equil. with the pseudooxazolones. In an attempt to use pseudooxazolones for the thiazolidine-oxazolone structure suggested for penicillin, Br was added to V and the product condensed with penicillamine (XI) in the presence of AcOK and AcOH. The low order of activity noted was probably due to BrCH2COCO2H which has an activity of 6 units per mg. against Gram-pos. organisms. X (1 g.) in 40 mL. pure AcOEt was hydrogenated at several atm. pressure in the presence of 2 g. active Raney Ni to IX, suggesting that the thiazolidine-oxazolone structure might be accessible by redn. of the corresponding pseudooxazolone. Ice-cold pyridine (20 mL.) in 65 mL. Me2CO was mixed with 1 g. (EtO)2CHCH(NHCOCHBrPh)CO2H and after 3 h., the mixt. was poured over crushed ice, extd. with CHCl3, washed with aq. NaHCO3, dried by passage through acid-washed Al2O3, and the filtrate was evapd., yielding 4.8 g. oily 2-benzylidene-4-(diethoxymethyl)pseudo-5-oxazolone, which failed to condense with XI. In another attempt, (EtO)2CHCH(NHCOCHClPh)CO2Me was condensed

with XI to give α-Me α-chlorobenzylpenicilloate (XII). On treatment of crude XII (5.2 g.) with a mixt. of 10.8 g. pyridine and 35.2 mL. Ac2O with shaking and cooling, a dark brown gum was formed, which, crystd. from Et2O at -50°, gave a "dehydropenicillin" (XIII), C16H16O4N2S, m. 90-5° (decompn.). Addnl. information in printed abstr.

CC 10 (Organic Chemistry)

L36 ANSWER 31 OF 32 HCA COPYRIGHT 2004 ACS on STN

48:40443 Original Reference No. 48:7242c-d Fertilizer. (Council of Scientific and Industrial Research). IN 47439 19540113 (Unavailable). APPLICATION: IN .

AB Kossier phosphate rock contg. 30.8% **P2O5** and 100 g. of 13.7% CaCO3 is treated with 142 g. of com. HCl (27% strength). The temp. developed during the reaction is sufficient for the disintegration of the phosphate rock and is maintained for 1 hr. with **mech. agitation.** (NH4)2SO4 (7 g.) is then added to the slurry thus obtained, and the mixt. is **stirred** by mech. means. The mass is then cured by dumping for 3 weeks. After this period 300 g. of a dry mass is obtained which is finally ground to a coarse powder. The product is a mixed N-P fertilizer and contains 15% **P2O5** and 7.4% N.

CC 15 (Soils and Fertilizers)

L36 ANSWER 32 OF 32 HCA COPYRIGHT 2004 ACS on STN

41:30992 Original Reference No. 41:6189g-i,6190a-i,6191a-i,6192a-c New transformation of crotonaldehyde. Flaig, Wolfgang Reichsamt Wirtschaftsausbau, Chem. Ber., Pruf. Nr. 093(PB52020), 1073-1108 (Unavailable) 1942. OTHER SOURCES: CASREACT 41:30992.

AB Derivs. of the enol form of MeCH:CHCHO were made by the dealkoxylation of acetals and condensation of the alkoxybutadiene with maleic anhydride and phthalic anhydride. MeCH:CHCHO (900 cc.) was added dropwise with stirring in 1.5 hrs. at not over -5° to 300 g. fused Na2SO4 in 1800 cc. abs. EtOH satd. with dry HCl. The lower layer was sepd., dried over Na2SO4, and distd., b14 72-4°. Abs. EtOH (1/3 vol.) was added to the distillate, the mixt. was cooled in an ice bath, 150 g. Ca(OH)2 added immediately, and 200-300 cc. Et2O at room temp. MeCHClCH2CH(OEt)2, b12 71°, obtained from the filtrate (yield 37%), refluxed 1 hr. with pulverized KOH in a Cu flask, gave 80% MeCH:CHCH(OEt)2 (I), b17 49°. Abs. EtOH (3000 g.), 75 g. concd. H2SO4, and 1500 g. MeCH:CHCHO was **stirred** 16 hrs. at 50° under a CO2 atm. NaOH (61 g.) in as little H2O as possible was added, and a **mixt.** of EtOH, **MeCH**:CHCHO, and H2O was distd. off at 40° and 90 mm. The filtrate was fractionated to yield 200 g. MeCH(OEt)CH2CHO, b14 40-70°, and 1300-1500 g. MeCH(OEt)CH2CH(OEt)2 (II), b14 80-1°. A condensation product (300 g.) of MeCH:CHCHO remained as a still residue. II, further

purified by refluxing and stirring with powd. KOH in a Cu flask, had d420 0.8750, nα20 1.40429, nβ20 1.41105, nγ20 1.41455, nD20 1.40620, and could be kept unchanged by adding a few drops of piperidine. A concd. aq. soln. contg. 40 g. NaOH was added at not over 20° to 1000 g. MeCH:CHCHO, 50 g. concd. H2SO4, and 1400 g. MeOH, and the filtrate was distd. at atm. pressure to remove 1000 g. of a **mixt.** of **MeCH**:CHCHO, MeOH, and MeCH(OMe)CH2CHO. Distn. of the upper layer of the remaining liquid gave 900-950 g. crude MeCH(OMe) CH2CH(OMe)2, which after purification by shaking with aq. NaHSO3, washing with dil. NaOH, H2O, drying over KOH, and distn., b7 44°, d420 0.9180, nα20 1.40073, nβ20 1.40735, nγ20 1.41083, nD20 1.40268. Catalysts for dealkoxylation of acetals were made from NaH2PO4.2H2O, Al2(SO4)3.18H2O, and MgSO4.2H2O by heating them until they had dissolved in their water of hydration, then until they had a doughlike consistency, passing them through a 2-mm. sieve to obtain granules, and heating at 350° and 15 mm. to completely remove the H2O. Catalysts contg. silicates were made by admixt. with 40°B.acte.e. water glass and drying 2.5 hrs. at 200°. Activated silica gels were prepd. by treating 45 g. of silica gel with 20 cc. of a 3% soln. of Ni(NO3)2, AlCl3, (NH4)2MoO4, TiCl3, or MnSO4 and drying in an oven 1 hr. at 200-50°. A small-scale app. for the conversion of trialkoxybutanes to alkoxybutadiene consisted of a 50-100 cc. heated Claisen flask equipped with dropping funnel, N inlet, manometer, and side arm delivering into an electrically heated tube 2.3 cm. in diam. packed for 30 cm. of its length with the catalytic agent. In 1 hr., 100 g. starting material could be swept through at 250-350° at a pressure difference of 15-20 mm. and condensed in receivers cooled in dry ice-Me2CO and in liquid air. A larger-scale app. somewhat similar in design permitted the conversion of 1 kg. or more of the starting material at the same rate. The alkoxybutadiene was recovered by washing the contents of the cooled receivers, drying over KOH, and distg. at 40 mm. Variation in catalyst (g.), temp., and time (hrs.) gave the following yields (%) of CH2:CHCH:CHOEt (III) from 100 g. I and II, resp.: I, 60 NaH2PO4, 350°, 1.5, 81; 50 Al2(SO4)3, 300-50°, 45, 52; 60 MgSO4, 350-70°, 1.5, 59; 35 B2O3, 350°, 1, 45. II, 50 Al2(SO4)3, 350°, 1.5, 3.0; 62 B2O3P2O5, 250°, 1.1, 56; 66 NaH2PO4, 320°, 2.5, 65; 69 SiO2 gel, 200°, 1.3, 56; 48 MgHPO4-water glass, 350°, 1.1, 74; 35 AlPO4-water glass, 300°, 1.0, 82; 30 fuller's earth, 300°, 0.6, 37; 10 Al2O3, 350°, 1.6, 69; 34 Al2O3-water glass, 350°, 1.0, 35; 25 C, 350°, 1.6, 72. MeCH:CHCH(OMe)2 (100 g.) passed over NaH2PO4 in 40 min. at 350° and 18 mm. gave 5 g. forerun, b87 29°, 24 g. CH2:CHCH:CHOMe, b87 44-6° (58%), 16 g. intermediate fraction b87 48-55°, 27.5 g. MeCH:CHCH(OMe)2 b87 57°, 2 g. still residue. Approx. the same yield of

CH_2:CHCH:CHOMe was obtained from MeCH(OMe)CH_2CH(OMe)2 with an activated SiO_2 gel. II (100 g.) and 50 g. Al_2O_3 gave 3.7 g. forerun, b13 53°, 5.1 g. MeCH(OEt)CH:CHOEt, b13 60-2°, 26.6 g. II, b13 76°, and a small amt. of a lower fraction, b. 74-6°. No semicarbazone was obtained from MeCH(OEt)CH:CHOEt but only a p-nitrophenylhydrazone, m. 172-3°, apparently identical with the p-nitrophenylhydrazone of MeCH(OEt)CH2CHO, m. 172-3°, since a mixed m.p. gave no depression and the mixed m.p. of the p-nitrophenylhydrazone of MeCH:CHCHO (m. 183-4°) and the p-nitrophenylhydrazone of MeCH(OEt)CH:CHOEt was 165-70°. The addn. of 0.1 mole Br during 20 min., with agitation, to 0.1 mole III in 75 cc. abs. Et2O caused the di-Br compd. to crystallize from soln. Na (0.1 g. atom) in 50 cc. abs. Et2O was added, the NaBr, EtOH, and Et2O were removed, and the residue distd. to give 6 g. CH2BrCH:CHCH(OEt)2, b0.3 74-5°, d420 1.2424, nα20 1.46997, nβ20 1.48159, nγ20 1.48899, nD20 1.47309, a colorless lachrymatory liquid when freshly distd., stable for some days when stored at -20°, rapidly decompg. at room temp. in air. On heating with K2CO3, 1 mole EtOH was evolved and the product crystd. at -4°. Br (0.2 mole) was added to 0.1 mole III in 100 cc. Et2O during 0.75 hr. at -70°, the Et2O was removed, the residue, needles m. above 30°, was again dissolved in Et2O, treated with 0.1 g.-atom Na in 50 cc. EtOH, and allowed to stand 20 hrs. at room temp. The NaBr, Et2O, and EtOH were removed, and somewhat impure CH2BrCHBrCHBrCH(OEt)2, b. 92-3° under very low pressure, was obtained. Bromosuccinimide (0.5 mole) was added in a finely powd. and carefully dried state to a vigorously **stirred** soln. of 0.1 mole III in 100 cc. abs. EtOH during 20-30 min. at 0-5°. After stirring 2 hrs. at room temp., the succinimide, EtOH, and Et2O were removed and by fractionation 64% CH2BrCH:CHCH(OEt)2, b0.001 47-51°, d420 1.2378, nα20 1.46884, nβ20 1.48064, nγ20 1.48743, nD20 1.47237, was obtained. CH2BrCH:CHCH(OEt)2 (42 g.) was slowly added to 122. KOH in 50 cc. MeOH at 0°. The mixt. was warmed 15 min. on the water bath, the KBr filtered off, and 5 vols. H2O added. The sepd. ethoxy acetal, washed with H2O, dried over KOH, and distd., gave 65% EtOCH2CH:CHCH(OEt)2, b1 52°, d420 0.9168, nα20 1.42512, nβ20 1.43344, nγ20 1.43781, nD20 1.42759. EtOCH2CH:CHCH(OEt)2 (25 g.), vaporized over 20 g. SiO2 gel in the small-scale app. at 250° and 14 mm., gave 11 g. of what was apparently EtOCH:CHCH:CHOEt, b4 52-4°. The originally colorless substance rapidly darkened and only a mol.-wt. detn. could be used to characterize it (found 154, calcd. 142). Methylene blue and other oxidation-reduction indicators were found to direct the reaction between an alkoxybutadiene and maleic anhydride to condensation and to inhibit the heteropolymerization which predominated in the absence of the catalyst. On heating 5 g. III

and 5 g. maleic anhydride in 100 cc. thiophene-free C6H6, in the absence and in the presence resp., of 1 mg. methylene blue, the % C6H6-insol. resin, C6H6-sol. resin, and cyclic addn. product (3-ethoxy-1,2,3,6-tetrahydrophthalic anhydride (IV), m. 38°) formed were: 10,0;40,14;40,84. IV was dissolved in dil. NaOH, the alk. soln. was acidified, extd. with Et2O, the Et2O soln. was dried, and the Et2O removed to yield 3-ethoxy-1,2,3,6-tetrahydrophthalic acid, m. 139-40° (xylene); the di-Me ester, obtained with CH2N2, m. below room temp., b14 120-1°. The effect of the addn. of 2 mg. of catalyst on the yield of IV from 10 g. III and 10 g. maleic anhydride was detd. In 100 cc. Et2O and in 100 cc. Me2CO soln., resp., the % yield was as follows: no catalyst, 20, 43; alizarin, 30, 55; anthraquinone, 19, 56; Bismarck Brown R, 39, -; crystal violet (carbinol base), 40, -; 2, 6-dichlorophenol-indophenol, 65, 92; dimethylnaphthoquinone, 31, -; fluorescein, 27, -; hydroquinone, -, 92; Indanthrene Blue B.C.S., 33, -; indanthrene khaki, 19, -; indigo disulfonate, -, 77; indigo trisulfonate, 32, 47; indigo tetrasulfonate, -, 67; indigotin, 28, 56; malachite green, 50, -; methylene blue (cryst.), 84, 76; Methylene Blue B Extra Merck, 65, 70; 1,4-naphthoquinone, 49, -; 1,2-naphthoquinone, 70, -; neutral red, 54, 85; phenanthrenequinone, 57, -; pyrogallol, 65, 85; Safranin T, 63, 77; thionine, 32, 94; thymol-indophenol, -, 70; toluylene blue, 45, 93. No relation was found between oxidation-reduction potential and the relative effectiveness of the catalyst. EtOCH:CHCH:CHOEt (43 g.), 3.1 g. maleic anhydride, and 2 g. methylene blue in 50 cc. thiophene-free C6H6 heated 3 hrs. on the water bath yielded 3 g. 3,6-diethoxy-1,2,3,6-tetrahydrophthalic anhydride, b. 126° at a very low pressure, a viscous oil which soon crystd., m. 91° (Et2O-petr. ether), converted to o-C6H4(CO)2O on heating at atm. pressure. 3-Methoxy-1,2,3,6-tetrahy drophthalic anhydride, m. 105° (from EtOAc), was obtained from the reaction at 125° of 10 g. CH2:CHCH:CHOMe, 10 g. maleic anhydride, 30 cc. (ClCH2CH2)2O. CH2:CHCH:CHOAc (57 g.) in 500 cc. C6H6 was added at once to 50 g. maleic anhydride in 500 cc. boiling C6H6 and the mixt. was heated 1.5 hrs. An insol. resin (7.7 g.) was sepd., 55 g. 3-acetoxy-1,2,3,6-tetrahydrophthalic anhydride (V), m. 58° (from Et2O), and 10.5 g. residue were obtained on distn. of the C6H6 soln. A similar expt. but in which 10 mg. methylene blue was present in the maleic anhydride soln. in C6H6 before the CH2:CHCH:CHOAc was added gave 7 g. resin and 71.5 g. (68.5%) V. V was also prepd. more directly from MeCH:CHCHO. Ac2O (660 g.), 350 g. MeCH:CHCHO, and 300 g. NaOAc were refluxed 5 hrs. at 160°. The distillate of the resulting filtrate (crude CH2:CHCH:CHOAc), 0.2 g. thionine, 100 g. maleic anhydride, and 200 cc. Me2CO were warmed 0.5 hr. on the water bath, and the lower-boiling material was removed at a bath temp. of 70° at 10 mm. pressure. V was obtained from the residue in 95% yield, based on maleic anhydride. Crude CH2:CHCH:CHOAc, thionine, maleic

anhydride, and Me2CO contg. 1 g. anhyd. NaOAc treated in a similar manner gave 25-35 g. (70-5%) 3,6-dihydrophthalic anhydride, b0.001 135°, m. 148°, converted to 3,6-dihydrophthalic acid, m. 150-3° (decompn.). 3,6-Dihydrophthalic anhydride was also obtained in almost quant. yield by heating 20 g. V in 5 cc. C5H5N 10 min. on the steam bath. 2,3-Dihydrophthalic acid (35 g.), m. 180°, was obtained by refluxing 50 g. V with 40 cc. concd. HCl, and was converted almost quantitatively by Ac2O to 2, 3-dihydrophthalic anhydride, m. 102°. V (42 g.) and 20 g. maleic anhydride were heated in a distg. flask to 200° to remove 11 g. AcOH. Crystals of 3,6-endo-vinylene-1,2,3,4-cyclohexane tetracarboxylic acid anhydride, m. 358° (decompn.), were obtained from the residue by washing with EtOAc; yield 20%. 23 references.

CC 10 (Organic Chemistry)

IT 1303-86-2, Boron oxide, B2O3
(as catalyst alone and with **P2O5** in dealkoxylation of acetals)

IT **1314-56-3**, Phosphorus oxide, **P2O5**
(catalysts from B2O3 and, in dealkoxylation of acetals)

=> d l37 1-37 ti

L37 ANSWER 1 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Flux method for manufacturing potassium phosphate titanate single crystal with suppressed flux inclusion

L37 ANSWER 2 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Bitumen modified with phosphorous compounds and a propylene polymer composition

L37 ANSWER 3 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Preparation of hydroxyapatite as stabilizer for suspension polymerization

L37 ANSWER 4 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Dispersants of antimony oxides and their compositions

L37 ANSWER 5 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Insoluble cyclodextrin polymer beads

L37 ANSWER 6 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Purification of sodium hexafluorosilicate

L37 ANSWER 7 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Clathrating anion-exchange resin

L37 ANSWER 8 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Clathrating cation-exchange resin

L37 ANSWER 9 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Ammonium phosphate compositions suitable for granular fire extinguishers

L37 ANSWER 10 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Treating used motor oil and synthetic crude oil

L37 ANSWER 11 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Treating used industrial oil

L37 ANSWER 12 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Ferric oxide-zinc oxide pigment

L37 ANSWER 13 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Low-halogen zinc ferrite pigments and their use

L37 ANSWER 14 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Phosphate ion absorbent

L37 ANSWER 15 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Filled unsaturated polyester resin compositions

L37 ANSWER 16 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI A process for dephosphorizing molten pig iron

L37 ANSWER 17 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Storage-stable, granulated silage additives

L37 ANSWER 18 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Dephosphorizing molten pig iron

L37 ANSWER 19 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Study of the decomposition kinetics of Karatau phosphorite fines by nitric acid and the rate of pulp filtration under pilot-plant conditions

L37 ANSWER 20 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Refining of steelmaking slag

L37 ANSWER 21 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Effect of the lump sizes of lime on its accumulation in the slag

L37 ANSWER 22 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Treatment of anatase ore

L37 ANSWER 23 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Manufacture of sodium tripolyphosphate

L37 ANSWER 24 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Peptides. LXXIII. Synthesis of the A chain of sheep insulin with exclusive use of acid labile protective groups

L37 ANSWER 25 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Mullite production

L37 ANSWER 26 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Converting crude siliceous bauxite to mullite

L37 ANSWER 27 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Flame-retardant polyurethane foams

L37 ANSWER 28 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Fly ash as a coagulant aid in water treatment

L37 ANSWER 29 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Pituitary growth hormone promoter

L37 ANSWER 30 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Colorimetric determination of arginine in protein acid hydrolyzates obtained from wheat flour

L37 ANSWER 31 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Isolation and characterization of soluble ribonucleic acid (RNA) from brewers' yeast

L37 ANSWER 32 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Chemical fertilizer

L37 ANSWER 33 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Proximity effects. XIX. Solvolysis of 4-cycloocten-1-yl brosylate with trifluoroacetic acid

L37 ANSWER 34 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Degradative studies on fucoidin

L37 ANSWER 35 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Assay of insulin in vitro by fibril elongation and precipitation

L37 ANSWER 36 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI The preparation and properties of equine pituitary gonadotropin

L37 ANSWER 37 OF 37 HCA COPYRIGHT 2004 ACS on STN
TI Nucleic acids. II. Nucleotidase from intestinal mucosa

=> d l37 17 cbib abs hitind

L37 ANSWER 17 OF 37 HCA COPYRIGHT 2004 ACS on STN
88:188524 Storage-stable, granulated silage additives. (Guano-Werke A.-G., Fed. Rep. Ger.). Belg. BE 852698 19770921, 12 pp. (French). CODEN: BEXXAL. APPLICATION: BE 1977-175969 19770321.

AB A granulated,noncaking silage additive contg. urea [57-13-6] and phosphates and some chlorides of Ca, Mg, and Na is manufd. by reacting a mixt. of urea and oxides and hydroxides and (or) carbonates of Mg, Ca, and Na, screening the product, and spraying with H3PO4 while mixing to form phosphates, which leave the mixer in the form of moist granules. For example, in the continuous app. described were ground, each h, 5000 kg recycled product screenings (<0.5 mm and >2.0 mm), 2540 kg urea (46% N), 170 kg dolomitic limestone (32.2% Ca, 19.5% Mg), 48 kg Ca(OH)2, 650 kg CaCO3, and 75 kg trace element mixt. The powd. mixt. was transported to a granulating drum rotating at 5 **rpm**, in which the mixt. was violently **stirred.** H3PO4 (50% **P2O5**) was sprayed at 1215 kg/h and then 50% NaOH was sprayed at 465 kg/h. The exothermic reaction provided an equil. temp. of 60° in the mixing area; the product with H2O content of 8% was dried to 4% at 90-110° and, the dried granules were screened and the fines recycled. The compn. of the product was: N (urea) 24.3, **P2O5** 12.1, H2O-sol. **P2O5** 6.0, Ca 11.4, Mg 0.7, and Na 2.7%; the pH of a 10% aq. suspension was 7.0, and granule size was 0.5-2.0 mm.

IC A01N

CC 17-5 (Foods)

=> d l38 1-46 ti

L38 ANSWER 1 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Manufacture of glass by stirring of molten glass by magnetic field

L38 ANSWER 2 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Glass-forming gel-coated pigments in printing pastes for enameling glass substrates, and their manufacture

L38 ANSWER 3 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Phosphoric ester surfactants for granular or **flowable** pesticide formulations

L38 ANSWER 4 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Iron- and lithium-promoted catalysts for the production of maleic anhydride

L38 ANSWER 5 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Conductive polymer with naphthothiophene structure

L38 ANSWER 6 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Silane production

L38 ANSWER 7 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Unsaturated acids and esters

L38 ANSWER 8 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Gelling agents for hydrocarbon compounds

L38 ANSWER 9 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Oxygen steel-smelting from pig iron of low phosphorus and sulfur contents

L38 ANSWER 10 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Storable and **flowable** long-chain alkyl phosphates

L38 ANSWER 11 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Phosphoric acid preparation by the Fison process

L38 ANSWER 12 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Apparatus comprising **stirred** reactor vessels for making phosphoric acid

L38 ANSWER 13 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Increasing available phosphate content of phosphate ore, for use as fertilizers

L38 ANSWER 14 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Terpenoids. XXVIII. Synthesis of humbertiol

L38 ANSWER 15 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Ammonium phosphate slurry fertilizer production by a continuous process

L38 ANSWER 16 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Pyridoxal 5'-orthophosphate

L38 ANSWER 17 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Polymerization of propylene in the presence of a Ziegler catalyst, water, and an amine

L38 ANSWER 18 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Composite fertilizer from phosphate, nitric acid, ammonia, and sulfur dioxide

L38 ANSWER 19 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Studies on peptides. VIII. Synthesis of two heptapeptides isolated from pituitary glands

L38 ANSWER 20 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Perfluorodecalin and octafluorodecalin synthesis

L38 ANSWER 21 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Pulplike fertilizers

L38 ANSWER 22 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Photosensitized oxygen transport to (+)-3-carene

L38 ANSWER 23 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Infrared absorbent aluminum phosphate coatings and method of manufacture

L38 ANSWER 24 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Fermentation of waste water from the brown-coal industry

L38 ANSWER 25 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI N-Methylol amide derivatives

L38 ANSWER 26 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Spectrophotometric determination of submicro quantities of ajmaline

L38 ANSWER 27 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Bridged polycyclic compounds. XXII. Carbenoid decomposition of nortricyclenone p-toluenesulfonylhydrazone

L38 ANSWER 28 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Nucleic acid components and their analogs. XIX. Synthesis of 3-methyl-6-azauridine 5'-phosphate and pyrophosphate

L38 ANSWER 29 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Vapor-phase fluorination of trichloroethylene with cobalt trifluoride and with manganese trifluoride

L38 ANSWER 30 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Ammonium citrate-soluble phosphate fertilizers containing mostly anhydrous dicalcium phosphate

L38 ANSWER 31 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Alkaline degradation of guaran and characterization of "β"-D-isosaccharinic acid

L38 ANSWER 32 OF 46 HCA COPYRIGHT 2004 ACS on STN

TI Improving the **flow** properties of highly ammoniated processed phosphate mixtures for multinutrient fertilizers

L38 ANSWER 33 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Polymerization reactions of itaconic acid and its derivatives

L38 ANSWER 34 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI The preparation of D-ribose-1-C14, D-arabinose-1-C14, and D-2-deoxyribose-1-C14

L38 ANSWER 35 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Heterocyclic vinyl eters. XVI. 2,5 Dimethyl-1,4-dithiadiene

L38 ANSWER 36 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Fluorinated carbon compounds

L38 ANSWER 37 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Pyrimidine nucleoside phosphates

L38 ANSWER 38 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Cyclopropene. I. The reaction of 2-bromocyclopropanecarboxylates with potassium tert-butoxide

L38 ANSWER 39 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Mechanism of fluorination. I. Fluorine sensitized oxidation of trichloro- and tetracbloroethylene

L38 ANSWER 40 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Grignard reagents of sulfones. III. Preparation and properties

L38 ANSWER 41 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI The controlled thermal decomposition of cellulose nitrate. I

L38 ANSWER 42 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Mechanism of oxidation. X. The conversion of tetrahydroharman alkaloids into derivatives of linear pyrroquinolones

L38 ANSWER 43 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Phosphate fertilizers

L38 ANSWER 44 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI 4-Benzyl-2,6-dimethylpyridine, 1-benzylisoquinoline, 9-benzylacridine, and certain relatives

L38 ANSWER 45 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Aluminum-alloy method for the gravimetric determination of total oxygen in plain carbon steels

L38 ANSWER 46 OF 46 HCA COPYRIGHT 2004 ACS on STN
TI Preparation of chlorine heptoxide

=> d l38 3,10,32 cbib abs hitind

L38 ANSWER 3 OF 46 HCA COPYRIGHT 2004 ACS on STN
108:217810 Phosphoric ester surfactants for granular or **flowable** pesticide formulations. Girardeau, Yvette; Ruffo, Georges; Segaud, Christian (Rhone-Poulenc Chimie SA, Fr.). Eur. Pat. Appl. EP 252824 A1 19880113, 29 pp. DESIGNATED STATES: R: AT, BE, CH, DE, ES, FR, GB, GR, IT, LI, LU, NL, SE. (French). CODEN: EPXXDW. APPLICATION: EP 1987-401564 19870703. PRIORITY: FR 1986-10159 19860711.

AB The surfactants comprise mixts. of alkoxylated phosphoric monoesters R1OROP(O)(OH)2 (I) and phosphoric diesters (R1ORO)2P(O)(OH)(II) [OR = C2-4 oxyalkylene moieties (1-80 repeating units); R1 = C8-20 alkyl or alkenyl, Ph, alkylphenyl, CHR4Ph; R4 = H, Ph, C1-4 alkyl]. The molar II/I ratio is ≥ 0.9. I + II represents ≥ 1% (molar) of the surfactant, the balance being the alkoxylated alc. R1OROH. **Stirred** 3 mol R2OROH was treated continuously (1h 15 min) with 1 mol **P2O5** at 43°, followed by stirring for 30 min and neutralization (pH 8) with triethanolamine to give a surfactant. Six g surfactant in 19.5 g monoethylene glycol was treated with 0.3g antifoam agent 416/R, 115.2 g water and 135 g plictran. The mixt. was processed in a ball mill and treated with 24 g 2% aq. Rhodopol 23, to give a **flowable** formulation.

IC ICM B01F017-00
ICS C07F009-09; A01N025-30

CC 5-6 (Agrochemical Bioregulators)
Section cross-reference(s): 46

L38 ANSWER 10 OF 46 HCA COPYRIGHT 2004 ACS on STN
77:164019 Storable and **flowable** long-chain alkyl phosphates. Roszinski, Hilmar; Klose, Werner; Noelker, Dieter (Knapsack A.-G.). Ger. Offen. DE 2114145 19721005, 9 pp. (German). CODEN: GWXXBX. APPLICATION: DE 1971-2114145 19710324.

AB Title compds. contg. 1.1-7.2:1 (HO)2P(O)OR (I)-HOP(O)(OR)2 (II) (R = n-C18H37 or mixts. of n-C16H33, n-C18H37, and n-C20H41) were prepd. and made storable by solidification of the molten mixts. with simultaneous scaling, keeping the scaly product .apprx.1 hr at >20° below the m.p., and controlling bulk height 5-12 cm, e.g. in a fluidized bed. Thus, **P2O5** was added to molten n-C18H37OH (III) at 90° and the mixt. **stirred** 5 hr at this temp. to give a 1.1:1 I-II mixt. (R = n-C18H37) contg. 4.4 III and 0.3 H3PO4. This mixt. was heated at 80°, scaled, and the scaly product passed 1 hr at ≤50° and bulk height .apprx.5 cm through a rotating open tube to give storable scaly

product.
IC C07F
CC 23-8 (Aliphatic Compounds)
IT 112-92-5 629-96-9 36653-82-4
(reaction of, with **phosphorus pentoxide**)

L38 ANSWER 32 OF 46 HCA COPYRIGHT 2004 ACS on STN
55:133435 Original Reference No. 55:25134f-i Improving the **flow** properties of highly ammoniated processed phosphate mixtures for multinutrient fertilizers. Karbe, Kurt; Boos, Wilhelm (Gewerkschaft Victor). DE 973443 19600218 (Unavailable). APPLICATION: DE .
AB Phosphate-HNO3 mixts. retain good **flow** properties during neutralization and subsequent treatment with NH3 and CO2 if 20-50% KCl (based on the amt. of crude phosphate) is added at pH 4-5. Only a fraction of the normally added amt. of stabilizer, esp. MgSO4, is necessary to ensure citrate soly. of the phosphate if KCl contg. MgSO4 is added. Thus, 25 kg. Morocco phosphate (33.4% **P2O5**) was processed with 34 l. of 52% HNO3. The liquid mass was treated with 2.88 kg. MgSO4. 7H2O (0.20 mole MgO/mole **P2O5**), neutralized (pH 7.5) with NH3, and treated with CO2 and NH3 at 60°. The mass became stiff and could not be **stirred**. Less than 1% CO2 was taken up. If the mass was only neutralized to pH 4.5, treated with 10 kg. KCl (59% K2O), treated with more NH3 to give pH 7.5, and treated with CO2 and NH3 at 60°, the mass remained a mobile liquid and contained finally N (total) 10.80, **P2O5**, (total) 9.01, **P2O5** (citrate-sol.) 8.86, H2O 20.0, K2O 6.5, CO2 3.55, and MgO 0.6%. The mixt. was treated with 30 kg. of 40% KCl, mixed with 3 times the amt. of previously dried material, and granulated to give a fertilizer contg. N 10.1, **P2O5** 8.18, **P2O5** (citrate-sol.) 8.05, and K2O 18.14%. In a similar example, no MgSO4.7H2O was used, and 6 kg. 59% KCl contg. 0.8% MgO was added to give a content of 0.020 mole MgO/mole **P2O5**. The final liquid mass contained N 11.7, **P2O5** 9.78, **P2O5** (citrate-sol.) 9.70, H2O 25.3, MgO 0.05, and CO2 3.40%.
NCL 16
CC 15 (Soils and Fertilizers)
IT Fertilizers
(ammoniated carbonated HNO2-treated phosphate, **flow** control in making, by KCl)

=> d l39 1-15 ti

L39 ANSWER 1 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Device for reduction of iron and vanadium in phosphoric acid solution

L39 ANSWER 2 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Glass preform for optical fibers

L39 ANSWER 3 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Catalytic oxidation of asphalt

L39 ANSWER 4 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Granular catalysts and catalyst supports

L39 ANSWER 5 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Separating solids suspended in a liquid

L39 ANSWER 6 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Ammoniated phosphoric acid

L39 ANSWER 7 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Gelatination during the decomposition of apatite by phosphoric acid

L39 ANSWER 8 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Granulation of mixed complex fertilizers

L39 ANSWER 9 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Specialized x-ray quantometer for the analysis of coarse-grained samples. Design of the quantometer model and certain results from the preliminary tests

L39 ANSWER 10 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Free-**flowing** fertilizer

L39 ANSWER 11 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI High analysis ammonium polyphosphate fertilizer

L39 ANSWER 12 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Granular diammonium phosphates

L39 ANSWER 13 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Sodium tripolyphosphate

L39 ANSWER 14 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Comparative consideration on metallurgical behavior of high-temperature coke from brown coal

L39 ANSWER 15 OF 15 HCA COPYRIGHT 2004 ACS on STN
TI Polymerization of isobutylene. II. Action of acid iron phosphates on a carrier

=> d l39 5,6 cbib abs hitind

L39 ANSWER 5 OF 15 HCA COPYRIGHT 2004 ACS on STN
79:7130 Separating solids suspended in a liquid. (Tate and Lyle Ltd.). Fr. Demande FR 2143201 19730309, 29 pp. (French). CODEN: FRXXBL. APPLICATION: FR 1972-22375 19720621.

AB Sugar juice, liquor, or syrup were clarified by a multi stage process involving addn. of a cationic sufactant as the primary flocculant, phosphatation-flotation during refining of the sugar, and addn. of an anionic flocculant based on polyacrylamide (I) (Taloflote) [9003-05-8], sepg. the secondary flocculated material by flotation, and clarifying the treated liquor by flocculation of the primary solid material contg. the coloring matter. Thus, to Jamacian sugar refusion liquor entering at **flow** rate 500 ml/min at 65.deg. Brix and 80.deg. was added phosphoric acid and lime to form the primary phosphate flocculant. Several samples with various concns. of **P2O5** from 100-600 ppm based on sugar solids were obtained. A control sample was also obtained before the phosphoric acid addn. The liq. was aerated by an agitator with diam. 0.91 m turning at 6000 **rpm**, and 10 ppm (based on sugar solids) I was added to give 0.1g flocculant/100 ml soln. After holding the liquor in the flocculator for a sufficient time, it was transferred to the separator and finally to the defecator to give **P2O5** 300 ppm, attenuation index 978, color after filtration through Millipore 973, turbidity index 0, and decoloration 33%, compared with 0, 2308, 1467, 841, and 0, resp., for the untreated liquor.

IC B01D; B03D; C13D

CC 44-2 (Industrial Carbohydrates)

L39 ANSWER 6 OF 15 HCA COPYRIGHT 2004 ACS on STN
75:97849 Ammoniated phosphoric acid. Legal, Casimer C., Jr. (W. R. Grace and Co.). Fr. Demande FR 2015048 19700612, 15 pp. (French). CODEN: FRXXBL. PRIORITY: US 19680805.

AB An ammonium phosphate was prepd. by reaction of H3PO4 and NH3 at high temps. in a tubular reactor. The heat of reaction was rapidly dissipated by the tubular reactor design. Thus, H3PO4 and anhyd. NH3 were 1st preheated to 135° before being reacted together in the reactor. The resulting reaction raised the temp. to 204-60°. The reaction product was led into a chamber and agitated with a rotating blade at 350 **rpm.** The NH3 and moisture were removed by a **flow** of air, and recycled. Retention time in the chamber was .apprx.5 min. The product contained 30.6% **P2O5** as polyphosphate which can be suitably used for fertilizer.

IC C01B; C05B

CC 20 (Fertilizers, Soils, and Plant Nutrition)

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=> d his l40-

     FILE 'HCA' ENTERED AT 15:44:05 ON 10 AUG 2004
L40            37 S L4(3A)L5
L41             1 S L40 AND (L6 OR L7 OR L8)
L42             1 S L40 AND L9
L43             5 S L40 AND L3
L44             0 S L40 AND (L28 OR L29)
L45           163 S L4(3A)(L6 OR L7 OR L8)
L46            10 S L45 AND L3
L47             3 S L45 AND L5
L48             0 S L45 AND (L28 OR L29)
L49             4 S L3(3A)L5
L50             2 S L3(3A)(L6 OR L7 OR L8)
L51            18 S (L41 OR L42 OR L43 OR L46 OR L47 OR L49 OR L50) NOT L36

=> d l51 1-18 cbib abs hitind
```

L51 ANSWER 1 OF 18 HCA COPYRIGHT 2004 ACS on STN

127:96616 Preparation and use of granular black iron oxide pigments. Koehler, Berndt-Ullrich; Eitel, Manfred; Linde, Guenter; Kunstmann, Herbert (Bayer A.-G., Germany). Ger. Offen. DE 19548418 A1 19970626, 5 pp. (German). CODEN: GWXXBX. APPLICATION: DE 1995-19548418 19951222.

AB The title pigments, stable and universally useable, are prepd. by adding 0.1-1.6% (based on oxide) binder to an Fe_3O_4 dispersion, drying, granulating, and heating at 80-650° in an inert or slightly reducing or oxidizing atm. A 40-70% Fe_3O_4 pigment paste was **stirred** with 1.0% **P_2O_5** (from Na polyphosphate) at room temp., spray dried, and heated under N in a rotary furnace at 400° for 30-60 min to give a pigment with relative (to Bayferrox 330) dispersibility 103%, coloristic values relative F 98% and b* -1.8, oxidn. stability (IMCO) 150°, and Fe(III)-Fe(II) ratio 1.9:1.

IC ICM C09C001-24
   ICS C01G049-02; C04B014-36; C04B040-00; C09D017-00; C08K003-22

ICA C08J003-20

CC 42-6 (Coatings, Inks, and Related Products)

IT 1314-56-3, **Phosphorus pentoxide**, uses
   7631-86-9, Silica, uses
   (binder; **prepn.** and use of granular black iron oxide pigments)

L51 ANSWER 2 OF 18 HCA COPYRIGHT 2004 ACS on STN

126:134471 Generation and relaxation of flow birefringence of high-viscous alkali phosphate glass melts. Brueckner, Rolf; Murach, Juergen; Hao, Shen (Institut fuer Nichtmetallische Werkstoffe, TU Berlin, Berlin, Germany). Journal of Non-Crystalline Solids,

208(3), 228-236 (English) 1996. CODEN: JNCSBJ. ISSN: 0022-3093.
Publisher: Elsevier.

AB It will be shown that there is a remarkable difference between the generation and relaxation behavior of the flow birefringence of alkali phosphate melts which is assumed to be in close connection to the stress relaxation modulus and to the recently defined stress generation modulus. This behavior is investigated under isothermal conditions within the high-viscosity range between 108 and 1012 Pa s by means of loading and unloading ternary sodium-lithium phosphate glass rods. The evaluation of the optical birefringence during loading and unloading exhibits two different generation and two relaxation times during the two processes in contrast to earlier investigations within the low-viscosity range <107 Pa.s where only one relaxation time was obsd. This result is in agreement with the structural conception of chains with increasing length and entanglement with decreasing temp. The dependence of the relaxation times on the chem. compn. has a max. at 50 mol% P2O5. The decrease of the relaxation times towards higher phosphate concns. points out a beginning of cross-linkage while towards lower phosphate concns. the length of the PO4-chains seems to be reduced. Of special interest is that the generation time is smaller than the relaxation time and decreases with increasing stress while the relaxation time increases with increasing stress. This behavior appears to be connected to orientation effects and to typical non-Newtonian flow (shear thinning effect).

CC 57-1 (Ceramics)

IT 1314-56-3, Phosphorus oxide (**P2O5**), properties
(glass; **generation** and relaxation of **flow** birefringence of high-viscous alkali phosphate glass melts)

L51 ANSWER 3 OF 18 HCA COPYRIGHT 2004 ACS on STN

117:212315 Preparation of 2-substituted indoles via Fischer indole **synthesis** using **phosphorus pentoxide** -methane sulfonic acid catalysts. Hughes, David L.; Zhao, Dalian (Merck and Co., Inc., USA). Brit. UK Pat. Appl. GB 2251856 A1 19920722, 48 pp. (English). CODEN: BAXXDU. APPLICATION: GB 1992-653 19920114. PRIORITY: US 1991-642778 19910118.

GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Title compds. [I; R, R11, R12 = H, halo, alkyl, alkenyl, alkynyl, CF3, cyano, NO2, N3, C(OH)R3R4, CO2R7, SR8, SOR8, SO2R8, SO2N(R9)2, OR9, N(R9)2, COR10, etc.; R1 = R, Q1; R2 = H, XR13; R3-R6 = H, alkyl; CR3R4, CR5R6 = C3-6 cycloalkyl; R7 = H, alkyl, (substituted)

PhCH2; R8 = CF3, alkyl, (substituted) phenyl(alkyl); R9 = H, COR10, alkyl, (substituted) phenyl(alkyl); R10 = H, CF3, alkyl, alkenyl, alkynyl, (substituted) Ph (alkyl); R13 = alkyl, alkenyl, (substituted) phenyl(alkyl); X = CO, CR3R4, SO2, bond; Y = O, NR9, CO, CR3R4, S, SO, SO2; Q = H, CO2R7, CONHSO2R8, NHSO2R8, SO2NHR9, CON(R9)2, CH2OH, tetrazolyl; m,v = 0, 1; n = 1-3; p = 0-3], were prepd. by treatment of hydrazone II with a catalyst contg. P2O5/MeSO3H (1:2-40) optionally in the presence of a cosolvent. Thus, 1-(4-chlorobenzyl)-1-[4-(2-quinolinylmethoxy)phenyl]hydrazine, MeCOCH2CMe2CO2Me, 4 Å sieves, HOAc, and PhMe were refluxed to give 91% hydrazone, which was **stirred** with **P2O5** /MeSO3H in sulfolane at 45-60° for 5d to give 85% indole III.

IC ICM C07D209-04

CC 27-11 (Heterocyclic Compounds (One Hetero Atom))

IT Fischer indole **synthesis** catalysts
(**phosphorus pentoxide**-methanesulfonic acid)

IT 100-63-0 107-87-9, 2-Pentanone 590-50-1 618-40-6 66372-99-4, Methyl 2,2-dimethyl-4-oxopentanoate 133165-83-0 133165-84-1 133165-85-2 133165-86-3 133166-03-7 133166-04-8 133166-05-9 133190-96-2
(Fischer indole **synthesis** reaction of, **phosphorus pentoxide**-methanesulfonic acid catalysts in)

IT 133165-87-4P 133165-99-8P
(prepn. and Fischer indole **synthesis** reaction of, **phosphorus pentoxide**-methanesulfonic acid catalysts for)

IT 133166-00-4DP, prepn. of, via Fischer indole **synthesis**, **phosphorus pentoxide**-methanesulfonic acid catalysts for
(prepn. of)

IT 91-55-4P 3484-18-2P 3623-86-7P 19869-53-5P 31151-19-6P 38136-74-2P 59931-85-0P 68051-17-2P 93549-89-4P 133165-90-9P 133165-91-0P 133165-93-2P 133165-94-3P 133165-95-4P 133165-96-5P 133165-97-6P 133165-98-7P 133166-01-5P
(prepn. of, via Fischer indole **synthesis**, **phosphorus pentoxide**-methanesulfonic acid catalysts for)

L51 ANSWER 4 OF 18 HCA COPYRIGHT 2004 ACS on STN

107:97274 Iron- and lithium-promoted catalysts for the production of maleic anhydride. Franchetti, Victoria Marie; Keppel, Robert Andrew (Monsanto Co., USA). Eur. Pat. Appl. EP 221876 A2 19870513, 12 pp. DESIGNATED STATES: R: DE, ES, FR, GB, IT. (English). CODEN: EPXXDW. APPLICATION: EP 1986-870157 19861027. PRIORITY: US 1985-791655 19851028; US 1985-791977 19851028.

AB Maleic anhydride is manufd. by the partial oxidn. of nonarom. hydrocarbons in the presence of a catalyst comprising P, V, O, and a

promoter component contg. Fe and Li. The catalyst has P-V atom ratio 0.50-2.00, (Fe + Li)/V atom ratio 0.0025-0.0080, Fe/V atom ratio 0.0010-0.0040, and Li/V atom ratio 0.0015-0.0040. The catalyst is prepd. by contacting a tetravalent V compd. and a P compd. with the promoter in an anhyd. alc. in the presence of anhyd. HCl to form a catalyst precursor which is dried, roasted, and calcined. A reactor was charged with 901.8 g 85.5% H3PO4, the acid stirred, and 343.4 g **P2O5** added, the soln. **stirred** for 20 min, and cooled to .apprx.20°. A second stirred reactor was charged with 8.3 L iso-BuOH, the alc. cooled to 10-15°, over 12 min the above-prepd. 100% H3PO4 added, the mixt. cooled, 963.0 g V2O5 stirred in, 1.35 g LiCl added, 0.96 g Fe powder added along with 1.0 L iso-BuOH. Anhyd. HCl (2,037.0 g) was added to the mixt. over a 4.67-h period, the soln. heated to reflux for 2 h, 5.4 L of distillate removed over 5.0 h, the mixt. refluxed for 1.38 h, 1.5 L distillate removed over a 2.36-h period, the turbid mixt. poured into Pyrex cake pans and placed in an oven at 140-150° for 5.5 h producing 2,225.0 g dried catalyst precursor which was ground, sieved, and roasted in a N-purged furnace to 260° over a 1-h period, and roasting continued for 3 addnl. hours, followed by gradual replacement of the N with air, and heating an addnl. 3 h to yield 1,980.0 g of black catalyst precursor powder. The dry powder was mixed with 1% powd. graphite, the mixt. pressed into pellets, and calcined. The catalyst was charged into a tubular reactor, heated to 200°, heated to 250° in **flowing** dry air over a 3.124-h period, the temp. reduced to 230°, and 1.8 vol.% H2O added to the dry **flowing** air. The reactor temp. was increased to 280° at 3°/h and 0.6 mol.% butane (I) was added to the **flowing** water-contg. air stream. The reactor temp. was increased to 400° at 1°/h and there maintained for 6 h. The catalyst P1.20V1.00Fe0.0015Li0.0030Ox was fed with I at 1.9 h-1 at 413-451°, resulting in I conversion 78.1% with maleic anhydride selectivity 69.8%.

IC ICM C07C051-215
ICS B01J027-198; B01J023-78

CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 27, 67

L51 ANSWER 5 OF 18 HCA COPYRIGHT 2004 ACS on STN

104:209445 Device for reduction of iron and vanadium in phosphoric acid solution. Ressel, Herbert; Westphal, Wilhelm (Hoechst A.-G. , Fed. Rep. Ger.). Ger. Offen. DE 3437689 A1 19860417, 9 pp. (German). CODEN: GWXXBX. APPLICATION: DE 1984-3437689 19841015.

AB Fe and V are reduced in phosphoric acid soln. in a rotating drum partially filled with granular reducing agent, with inlets for the H3PO4, granular reducing agent, and an inert gas and an outlet for the reaction product, e.g., in the form of an overflow tube from the

top of the drum. Ferrophosphorus, FeSi, Fe oxides, or red P may be used as the granular reducing agent. Thus, a 0.8-m diam., 3-m long drum contg. 6 baffle plates was filled with 1.6 ton broken ferrophosphorus (<10 mm, fine particles <0.5 mm 3.8%, compn. P 22.9, Si 4.7, Ti 2.4%, balance Fe) and rotated at 2 **rpm**, hot H3PO4 (contg. **P2O5** 27.9 wt.%, V5+ 123 ppm, total Fe 0.2 and Fe2+ 0.02%) was fed at 7 m3/h and 80-90° through an inlet with a stopper screw and **flowed** out through the overflow to the bottom of a container with a double-arm stirrer where it reacted with the finely divided ferrophosphorus particles, solids settled out, and the clear liq. was released from the top of the container and collected in a vessel from which a reaction product was removed contg. total Fe 0.23, Fe 2+ 0.22, and V4+ 115 ppm.

IC ICM C01G001-00
ICS C01G031-00; C01G049-00

CC 49-1 (Industrial Inorganic Chemicals)
Section cross-reference(s): 47

L51 ANSWER 6 OF 18 HCA COPYRIGHT 2004 ACS on STN

102:26528 Epoxy phosphoric acid adducts. Lottermoser, Manfred (Fed. Rep. Ger.). Ger. Offen. DE 3304379 A1 19840809, 11 pp. Addn. to Ger. Offen. 3,208,748. (German). CODEN: GWXXBX. APPLICATION: DE 1983-3304379 19830209.

AB Compns. useful in rust conversion, coatings, lubricants, etc. are prepd. by reaction of unsatd. materials (e.g. oils, olefins, polystyrene waste) with peroxides and P2O5. Thus, adding 153 mL 30% H2O2 in portions to 100 g linseed oil and 40.4 g **P2O5** **stirred** at 120-130° gave a viscous, honey-yellow product sol. in aq. alkalies and iso-PrOH. Aq. solns. of alkali or alkanolamine salts were useful in rust prevention, and iso-PrOH solns. were good rust conversion coatings for rusted steel.

IC C07F009-09; C09D005-08; C10M003-40; C10M001-46; B01F017-14; C08K009-04; B05D007-14; B05D007-26; C23F011-16; E04B001-62

CC 42-10 (Coatings, Inks, and Related Products)

IT Corrosion inhibitors
(olefin-hydrogen peroxide-**phosphorus pentoxide** reaction **products** as)

IT Coating materials
(rust-converting, olefin-hydrogen peroxide-**phosphorus** **pentoxide** reaction **products** as)

IT 111-66-0D, reaction products with hydrogen peroxide and phosphorus pentoxide 143-28-2D, reaction **products** with **phosphorus pentoxide** and hydrogen peroxide **1314-56-3D**, reaction **products** with unsatd. compds. and hydrogen peroxide 7722-84-1D, reactions products with olefins and phosphorus pentoxide 13598-52-2D, reaction products with olefins
(anticorrosive compns. contg.)

L51 ANSWER 7 OF 18 HCA COPYRIGHT 2004 ACS on STN
100:88051 Mathematical model of continuous decomposition of potassium chloride with polyphosphoric acid. Kubaev, A. Kh.; Namazov, Sh. S.; Radzhabov, R.; Beglov, B. M.; Kamalov, K. M. (Inst. Khim., Tashkent, USSR). Uzbekskii Khimicheskii Zhurnal (6), 59-63 (Russian) 1983. CODEN: UZKZAC. ISSN: 0042-1707.
AB A math. model is developed, on the basis of exptl. studies in 2 graphite reactors connected in parallel, for the decompn. of KCl with polyphosphoric acid. An increase in temp. and concn. of the polyphosphoric acid increases the coeff. of decompn. of KCl. The optimal conditions for the reaction are: temp. 245-250°, concn. of the polyphosphoric acid 76.7% **P2O5** and the mass **flow** rate of KCl at P2O5:K2O ratio of 1:0.5 is 35-45 g/h for a reactor vol. of 2.85 + 10-6 m3. Under these conditions, the coeff. of decompn., concn. of **P2O5** in the **product** , and the degree of conversion of P2O5 are 98.3-98.4, 59.20-59.65, and 79.5-80.1%, resp.
CC 49-10 (Industrial Inorganic Chemicals)

L51 ANSWER 8 OF 18 HCA COPYRIGHT 2004 ACS on STN
89:162274 Preparation of potassium sulfopolyphosphates based on the reaction of potassium chloride with sulfopolyphosphoric acid. Namazov, Sh. S.; Arifdzhanov, S. M.; Adylova, M. R. (Inst. Khim., Tashkent, USSR). Uzbekskii Khimicheskii Zhurnal (4), 3-7 (Russian) 1978. CODEN: UZKZAC. ISSN: 0042-1707.
AB Highly-concd. Cl-free P-K fertilizers were obtained by reacting KCl with thermal sulfopolyphosphoric acid (81.56% P2O5) prepd. according to US Patent No. 334005 (1967). Increasing the temp. (100-350°) and the P2O5/K2O ratio (1:0.5, 1:0.668 and 1:0.8) affected significantly the Cl- evolution; it reached 99.75% at 250° and P2O5/K2O ratio 1:0.5. The products of KCl decompn. obtained at the former **P2O5**/K2O ratio **formed** a highly mobile, **flowing** melt easily removable from the reactor when hot. Total P in the products increased and H2O-sol. P decreased at all P2O5/K2O ratios with increasing decompn. temp. In the products 7-8 phosphate forms were found. K sulfopolyphosphate obtained at 200-350° contained trimeta, tetrameta, and pentameta phosphate anions. The mol. compn. of acid K sulfophosphates obtained at various P2O5/K2O ratios and temp. is presented.
CC 19-5 (Fertilizers, Soils, and Plant Nutrition)
Section cross-reference(s): 49

L51 ANSWER 9 OF 18 HCA COPYRIGHT 2004 ACS on STN
87:210147 Calculation of the deposition of a film of silicon dioxide and **phosphorus pentoxide** during the laminar **flow** of a gas mixture in a horizontal flat channel. Popov,

V. P.; Skoropanov, Yu. S. (USSR). Teplo- Massoobmen Dvukhfaznykh Sist. Fazovykh Khim. Prevrashch., 95-111. Editor(s): Ganzha, V. L.; Vinogradov, L. M.; Grushetskaya, S. M. Akad. Nauk BSSR, Inst. Teplo- Massoobmena: Minsk, USSR. (Russian) 1976. CODEN: 36LDAD.

AB A math. model was presented of P2O5 and SiO2 deposition during the oxidn. reaction of PH3 and SiH4 in the gas phase and in the reaction zone adjacent to the heated gas layer. Sep. particles of SiO2 and **P2O5 form** in that zone. At the oxidn. temp. 300-600°, the forming oxides are overcooled and susceptible to the formation of complexes. Therefore, the simultaneous formation of sep. oxide mols. and of complexes occurs. The diffusion coeffs. of the complexes are lower than the coeffs. of oxide particle diffusion. The results of the calcns. qual. agree with known exptl. data.

CC 76-13 (Electric Phenomena)
Section cross-reference(s): 78

L51 ANSWER 10 OF 18 HCA COPYRIGHT 2004 ACS on STN
83:193092 Azabicyclo derivatives. Kimura, Michio; Nakajima, Takeshi; Inaba, Shigeho; Yamamoto, Hisao (Sumitomo Chemical Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 50049297 19750501 Showa, 6 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1973-99969 19730904.

GI For diagram(s), see printed CA Issue.

AB Azabicyclo derivs. I (R1 to R5 = H, alkyl, OH, hydroxyalkyl, alkoxy, cyano, NH2, halo, CO2H, alkanoyl, aryl; R6 to R9 = H, alkyl) were prepd. by cyclization of tetrahydropyridines (II) or their salts with acids. Thus, 20 g 1-(3,3-dimethylallyl)-4-methyl-1,2,5,6-tetrahydropyridine was **stirred** with H3PO4-**P2O5** (**prepd**. from 270 g 85% H3PO4 and 214 g P2O5) 4 hr at 135-40° under N to give 4,4,6-trimethyl-1-azabicyclo[3.3.1]non-6-ene. I also prepd. were (R1 to R9 given): H, H, H, H, H, H, H, H, Me, Me; Me, Me, Me, H, H, H, H, Me, Me; H, Me, Me, H, H, H, H, Me, Me; and H, H, Me, H, H, H, H, Me, Et.

IC C07D; A61K

CC 27-17 (Heterocyclic Compounds (One Hetero Atom))

L51 ANSWER 11 OF 18 HCA COPYRIGHT 2004 ACS on STN
83:61882 Coating agents for polyolefin substrates. Miyakawa, Norio; Sato, Mitsuo; Kobayashi, Takashi (Mitsubishi Rayon Co., Ltd.). Jpn. Kokai Tokkyo Koho JP 49039623 19740413 Showa, 7 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1972-83657 19720823.

AB Polyolefin substrates are coated with a resin compn. comprising the reaction product of a hydroxy group-contg. polyester with one or more (meth)acrylic acids or their derivs., phosphates, prepd. by reaction of polyphosphoric acid or P2O5 with ethylenically-unsatd. hydroxy group-contg. monomer, and solvent, and irradn. cured, to give a coating film with good hardness and chem. resistance. Thus, 260 g of a polyester (prepd. from phthalic anhydride and ethylene

glycol) was heated 3 hr at 95° with acrylic acid 180, cyclohexane 60, p-toluenesulfonic acid 5, and hydroquinone 8 g to give a polyester polyacrylate in 80% yield. The reaction product of 2-hydroxyethyl methacrylate 520, hydroquinone 1, and **P2O5** 30 g was **stirred** with the polyester polyacrylate 520, Et acrylate 55, vinyltoluene 100, and TiO_2 160 g to give a white enamel, which was coated (2 mm thickness) on a polypropylene molding piece, and irradiated with electron beams to give a coating film with pencil hardness H, and good chem. resistance and peel strength.

NCL 24H02; 24F0; 24C01

CC 42-2 (Coatings, Inks, and Related Products)

IT 2-Propenoic acid, 2-methyl-, 2-hydroxyethyl ester, reaction **products** with **phosphorus pentoxide**
(polyester acrylate coatings contg., radiation-curable)

L51 ANSWER 12 OF 18 HCA COPYRIGHT 2004 ACS on STN

70:60839 Anticariogenic compositions. Muhler, Joseph C. (Indiana University Foundation). S. African ZA 6801030 19680710, 41 pp. (English). CODEN: SFXXAB. PRIORITY: US 19670307.

AB The title compns. were prepd. by the reaction of urea with P_2O_5 in an aq. environment in molar ratios of 2:1, 4:1, and 8:1. The compns. exhibited a high degree of anticariogenic effectiveness in the presence of sugar or in comestibles or in sugar-contg. comestibles. Thus, 30.0 g. chem. grade urea in 30 ml. redistd. H_2O in a 50-60° const. temp. bath treated within 5 min. with 71.0 g. **P2O5**, the mixt. **stirred** until viscous, maintained 48 hrs. at 50°, and dried 96 hrs. over $CaCl_2$ gave 99% product comprising mainly urea pyrophosphate (I). Similarly, the reaction of urea and P_2O_5 in a molar ratio of 4:1 as above gave mainly dimerized urea carbamido pyrophosphate (II), m. 110-16°, as well as minor amts. of urea carbamido pyrophosphate, diurea pyrophosphate, dimerized diurea pyrophosphate, urea orthophosphate, and carbamido phosphoric acid. Also similarly, the reaction of urea and P_2O_5 in a molar ratio of 8:1 as above gave mainly tetraurea pyrophosphate (III), m. 89.5-95.5°, as well as minor amts. of diurea dicarbamido pyrophosphate, diurea orthophosphate, and urea carbamido phosphate. II and III were characterized by x-ray diffraction methods; I is already known. Tests on rats measuring the redn. in enamel soly. indicated that the cariogenic potential of sugars and also of artificial sweeteners was reduced by incorporating at least 0.05% I, II, or III by wt. of the sugar, II and III being esp. effective. The LD_{50} was detd. for II and III as 5.60 and 8.10 g./kg. resp., compared with 9.69 g./kg. for NaH_2PO_4.

CC 63 (Pharmaceuticals)

IT **1314-56-3**
(reaction **products** with urea)

L51 ANSWER 13 OF 18 HCA COPYRIGHT 2004 ACS on STN
68:82416 Silicon elements for high-voltage rectifiers and for thyristors. (Associated Electrical Industries Ltd.). Fr. FR 1487219 19670630, 6 pp. (French). CODEN: FRXXAK. PRIORITY: GB 19650722.

AB Multilayer Si single-crystal semiconductor elements are prepd. by epitaxial deposition, covered with a layer of silicophosphate glass and heated in order to remove impurities (e.g. Cu by diffusion and absorption in this layer). A simple app. for this process comprises a silica-glass tube and a system of inlets and outlets making it possible to reverse the flow direction and to change the compn. of reaction gases without interrupting the process. The desired p or n layers are deposited on highpurity Si single-crystal plates resting on a quartz-covered graphite block and heated, preferably by induction. Doped layers result from a thermal decompn. of a mixt. of anhyd. H and suitable volatile compds. of Si and the doping element at 900-1300° (e.g., a good Si layer results at a growth rate of 2.5 μ/min. at 1250° and a flow rate of 1 l./min., from a mixt. of H with 2 mole % SiCl4). After the epitaxial deposition has been completed, a silicophosphate glass layer is produced on the elements by **flowing P2O5** vapors through the tube (resulting from a mixt. of O and PH3, or from passing a dry gas (O, N, Ar) over P2O5 heated to 200-800°) at 1000-1300°, or by application of a 2-methoxyethanol soln. of P2O5 and subsequent drying and heating to 1000-1300°. The elements are usually heated 1-3 hrs. Typical parameters are: temp. of P2O5 container 450°, Si element temp. 1200°, heating time 2 hrs., cooling rates 360°/hr. to 750° and 100-200°/min. from 750° to room temp. The diffusion of P into the element is much slower than that of the impurities into the glass layer; nevertheless a P-doped n-layer results on the surface, which can easily be removed chem. or mech., or preserved if an n-layer is needed on the surface. Multilayer elements are produced in this way for potentials of 2-5 kv. (depending on the thickness of the corresponding layer, which is 0.2-0.5 mm.) with a minority-carrier lifetime of 10-50 μsec.

IC H01L; B01J

CC 71 (Electric Phenomena)

IT Electric rectifiers
(silicon controlled and high-voltage, epitaxy and gettering by phosphorus oxide (**P2O5**) in **manuf.** of)

L51 ANSWER 14 OF 18 HCA COPYRIGHT 2004 ACS on STN
60:21518 Original Reference No. 60:3756f-g Phosphoric acid anhydride. Klein, George I.; Newby, Ralph E.; Post, Leo B. (Stauffer Chemical Co.). US 3100693 19630813, 5 pp. (Unavailable). APPLICATION: US 19600617.

AB P2O5 is continuously condensed in a fluidized bed of P2O5 in an app.

providing an endless recirculating dry arm. Thus, P2O5, contg. 11-170 p.p.m. H2O vapor, produced in a combustion chamber, was introduced at 510-70° into the interior of a fluidized bed of granular P2O5 at 129° and with a d. of 40 lb./cu. ft. A free-**flowing**, dustless **form** of hexagonal **P2O5** in the shape of small spheres or beads with a bulk d. of 67-74 lb./cu. ft. was produced at a rate of 5 lb./hr./cu. ft. of fluidized bed. The fluidizing gases were passed progressively in the closed system, (1) through a cyclone separator, which removed the larger particles of P2O5 and returned them to the bed, (2) through a scrubber using superphosphoric acid (77% P2O5 as the scrubbing medium) which removed the fines, and (3) a cooler, before being returned to the fluidized bed. As the P2O5 condensed on the P2O5 bed, the bed product was withdrawn continuously at the same rate.

NCL 023262000

CC 17 (Industrial Inorganic Chemicals)

L51 ANSWER 15 OF 18 HCA COPYRIGHT 2004 ACS on STN

56:24851 Original Reference No. 56:4654d-i,4655a-b Lignans. I. Acylation in polyphosphoric acid as a route to intermediates. Ayres, D. C.; Denney, R. C. (John Cass Coll., London). Journal of the Chemical Society, Abstracts 4506-9 (Unavailable) 1961. CODEN: JCSAAZ. ISSN: 0590-9791. OTHER SOURCES: CASREACT 56:24851.

AB Phenols and their ethers with alkoxybenzoic acids in polyphosphoric acid (PPA) gave esters and benzophenones, resp., the latter being intermediates in prospective syntheses of phenyltetrahydronaphthalene lignans. Phosphorylation was found to affect the course of some reactions. PPA was **prepd.** by mixing **P2O5** 8 with 90% H3PO4 (d. 1.75) 5 parts and stirring 30 min. at 85° before use. Vanillic acid (I) (5.0 g.) and 4.1 g. veratrole (II) stirred into PPA (from 50 g. P2O5) and the soln. kept 30 min. at 80-3° and poured into 250 ml. ice H2O gave 8.0 g. 4-hydroxy-3,3',4'-trimethoxybenzophenone (III), m. 142-3° (1:1 EtOH-H2O), ν 3300 and 1669 cm.-1 III (1.0 g.) in 3% aq. NaOH shaken 15 min. at room temp. with 1.0 g. Me2SO4 gave 0.81 g. [3,4-(MeO)2C6H3]2CO, m. 144° (EtOH), ν 1635 cm.-1 3,4,5-(MeO)3C6H2CO2H (IV) (4.6 g.) and 3.0 g. III in PPA (from 35 g. P2O5) treated as above gave 6.9 g. 3,4,5-(MeO)3C6H2COC6H3(OMe)2-3,4, m. 118-19° (EtOH), ν 1630 cm.-1 I (5 g.) and 3.2 g. PhOMe in PPA (from 50 g. P2O5) gave 8 g. 3,4-MeO(HO)C6H3COC6H4OMe-4 (V), m. 109-10°, ν 3300 and 1635 cm.-1 V (1.0 g.) methylated with 0.8 g. Me2SO4 as above and the mixt. heated 30 min. on a H2O bath gave 0.80 g. 3,4-(MeO)2C6H3COC6H4OMe-4, m. 98-9° (1:1 EtOH-H2O), ν 1636 cm.-1 IV (10.6 g.) and 8.4 g. 1,2,3-C6H3(OMe)3 (VI) in PPA (from 88 g. P2O5) treated as above gave 16.3 g. 2,3,4-(MeO)3C6H2COC6H2(OMe)3-3,4,5 (VII), m. 121° (aq. EtOH), ν 1650 cm.-1

1,2-CH2O2C6H4 (0.50 g.) in PPA stirred 2 hrs. at 20-2° and
the mixt. dild. with H2O gave 2 polymeric products, one (0.26 g.) by
Et2O extn. and the other (0.11 g.) by subsequent C6H6 extn.
o-C6H4(OH)2 (VIII) (13.0 g.) and 25.0 g. IV in PPA (from 200 g.
P2O5) heated and **stirred** 40 min. at 85° and
poured into 400 ml. ice H2O gave 33 g. 2-HOC6H4O2CC6H2(OMe)3-3,4,5
(IX), m. 178-9° (1:1 EtOH-H2O), ν 3450 and 1736 cm.-1
Repetition of this expt. with 11.0 g. VIII and 42.4 g. IV and the
product (35 g.) washed with aq. NaHCO3 gave 30 g. IX. VIII and
4,3,5-HO(MeO)2C6H2CO2H (X) (each 0.05 mole) treated as above gave
75% 4,3,5-HO(MeO)2C6H2CO2C6H4OH-2, m. 212° (1:1 EtOH-H2O),
ν 3350 and 1725 cm.-1 1,2-CPh2O2C6H3 (Mason, CA 39, 40642) (3.0
g.) and 2.32 g. IV in PPA (from 25 g. P2O5) treated as above (35
min. at 85°) gave 4.9 g. IX, m.p. and mixed m.p.
176-7° (4:1 EtOH-H2O). VIII and IV (each 0.02 mole) refluxed
5 hrs. in 40 ml. Et2O contg. 45% BF3, the mixt. cooled, treated with
100 ml. H2O, the Et2O distd., the hot liquor decanted from 2 g.
insol. oil, and the latter crystd. from 1:1 EtOH-H2O gave IX, m.
179°; methylation of 1.0 g. IX gave 0.70 g.
2-MeOC6H4O2CC6H2(OMe)3-3,4,5, m. 113° (EtOH), an identical
compd. being obtained on methylation of X prepd. above. VIII (2.5
g.) and 10.5 g. 3,4,5-(MeO)3C6H2COCl kept molten 2 hrs., the melt
cooled, and the solid washed with aq. NaHCO3 gave 11.4 g.
o-C6H4[O2CC6H2(OMe)3-3,4,5]2 (XI), m. 154° (1:1 C6H6-petr.
ether). XI (4.0 g.) in 70 ml. PhNO2 heated 4 hrs. on a steam bath
with 3.5 g. AlCl3 and the mixt. cooled, acidified with 20 ml. 5N
HCl, and steam distd. gave 2.8 g. X, m. 203°; VIII was
present in the steam distillate (FeCl3 test). Gallic acid (XII)
(4.0 g.) and 3.95 g. VI **stirred** in PPA (from **P2O5**
), the soln. kept 1 hr. at 90°, poured into 100 ml. ice H2O,
the ppt. (0.5 g.) filtered off, the filtrate extd. with Et2O (the
ext. contained 2.2 g. material; the ppt. and the extd. material were
a mixt. of XII and VI, predominantly VI), the aq. filtrate refluxed
2 hrs. with 200 ml. 2N HCl, and the product isolated with Et2O gave
2.7 g. 3,4,5-(HO)3C6H2COC6H2(OMe)3-2,3,4, m. 181-2° (1:1
EtOH-H2O), ν 3300 and 1663 cm.-1, methylation giving 83% VII, m.
121-2°. 2-MeOC6H4OH (XIII) and I (each 0.03 mole) in PPA
(from 50 g. P2O5) heated 30 min. at 80°, poured into 250 g.
ice H2O, and the mixt. worked up gave 74% recovered I and 60%
recovered XIII; no ketone was detected.

CC 29 (Noncondensed Aromatic Compounds)

L51 ANSWER 16 OF 18 HCA COPYRIGHT 2004 ACS on STN
44:17709 Original Reference No. 44:3517h-i,3518a-b
Chloroalkanephosphonyl and -thiophosphonyl dichlorides. Woodstock,
Willard H. (Victor Chemical Works). US 2495799 19500131
(Unavailable). APPLICATION: US .

AB Olefins with a terminal double bond and having only 1 alkyl group on

the 2-C atom add PCl5 in the sense -C(PCl4)-CCl; the **products** with **P2O5** and P2S5 give, resp., 1-chloroalkane-2-phosphonyl or thiophosphonyl dichlorides. The products may be esterified, amidated, or hydrolyzed to the corresponding derivs. of the 1-chloroalkane-2-phosphonic or thiophosphonic acids. 1-Butene (125 g.) in 1200 ml. C6H6 treated at 0-5° with 417 g. PCl5, stirred 6 hrs., treated with 106 g. **P2O5, stirred** at room temp. 5 hrs., at 35° 4 hrs., and at 50° 9 hrs., filtered, concd. in vacuo, and distd. gave 224 g. EtCH(POCl2)CH2Cl, b18 116-23°. Similarly, 81.5 g. 1-pentene in C6H6 with 208.5 g. PCl5, followed by 55 g. P2O5 (2 hrs. at room temp., 3 hrs. at 35°, and 3 hrs. at 50°), gave PrCH(POCl2)CH2Cl, b20 130-2°, m. 39-42°, d25 1.319. Passage of 160 g. propene into 1200 ml. benzene contg. 208.5 g. PCl5 for 11 hrs. at 20°, followed by 55 g. P2O5 and treatment as given above, resulted in MeCH(POCl2)CH2Cl, b. 190-218°. PrCH(POCl2)CH2Cl (150 g.) and 200 g. BuOH stirred 25 min. at 25-30°, then 6 hrs. at 55° until HCl evolution stopped, gave PrCH[PO(OBu)2] CH2Cl, b4 154-62°, d25 1.106, m. below -70°. The esters are useful as oil-treating agents, flameproofing agents for textiles, and as fire-retarding plasticizers. Cf. C.A. 44, 7499e.

CC 10 (Organic Chemistry)

L51 ANSWER 17 OF 18 HCA COPYRIGHT 2004 ACS on STN

41:30993 Original Reference No. 41:6192c-g Intermolecular dehydrations by means of **phosphorus pentoxide**. I. **Preparation** of substituted acetophenones. Kosolapoff, G. M. (Monsanto Chem. Co., Dayton, O.). Journal of the American Chemical Society, 69, 1651-2 (Unavailable) 1947. CODEN: JACSAT. ISSN: 0002-7863.

AB A no. of aromatic compds. have been condensed with AcOH to form the corresponding acetophenones, using about 0.5 mole P2O5 per mole AcOH. m-C6H4Me2 (I) (106 g.) and 60 g. AcOH, treated with 3 g. celite and 71 g. **P2O5** and **stirred** and refluxed 2 hrs., give 52 g. 2,4-Me2C6H3Ac2 (II), b20 120-5°, and 10 g. 1,2,3,4- or 1,2,4,5-Me2C6H2Ac2 (III), b5 100-5°; after heating 30 min., the yields were 53 g. II and 12 g. III; 53 g. I, 60 g. AcOH, and 71 g. P2O5 give after 2 hrs. 20 g. II, 30 g. III, and 20 g. residue. PhMe (92 g.), 60 g. AcOH, 71 g. P2O5, and 3 g. celite, refluxed 2 hrs., give 15 g. p-MeC6H4Ac, b20 115-20°. Cyclohexylbenzene similarly gives a small yield of cyclohexylacetophenone, b10 150-60°. PhOMe (108 g.), 71 g. P2O5, and 5 g. celite, treated at reflux temp. (30 min.) with 60 g. AcOH, give 30 g. PhOMe, 15 g. p-MeOC6H4Ac (IV), 30 g. Ac2C6H3OMe (V), b30 157-70°, and 70 g. residue; 324.4 g. PhOMe, 90 g. AcOH, 107 g. P2O5, 200 cc. C6H6, and 10 g. celite, refluxed 90 min., give 106.5 g. IV, 36.7 g. V, and 15.7 g. residue. PhOEt (122 g.), 60

g. AcOH, 71 g. P2O5, and 3 g. celite, refluxed 2 hrs., give 50 g. p-EtOC6H4Ac (VI) and 35 g. Ac2C6H3OEt (VII), b5 170-240°; 244 g. PhOEt, 60 g. AcOH, 71 g. P2O5, and 5 g. celite in 200 cc. C6H6, refluxed 75 min., give 152 g. PhOEt, 95 g. VI, and 20 g. VII; crystd. from EtOH, VII forms pale yellow plates, m. 141.5-2°. 1,3,5-C6H3Me3 (100 g.), 120 g. AcOH, 171 g. P2O5, and 5 g. celite, heated 90 min., give 82.5% 2,4,6-Me3C6H2Ac, b1 100-2°.

CC 10 (Organic Chemistry)

L51 ANSWER 18 OF 18 HCA COPYRIGHT 2004 ACS on STN

34:32171 Original Reference No. 34:4895c-f Treating hydrocarbon oils such as crude gasoline distillates with phosphorus pentoxide. Sachs, Albert P. (Petroleum Conversion Corp.). US 2191043 19400220 (Unavailable). APPLICATION: US .

AB An arrangement of app. is described, and a method for the treatment of low-boiling material such as a crude gasoline distillate with P2O5 to effect purification and utilize olefinic compds. present, which involves prepg. the material for treatment by removing therefrom substances sol. in dil. acid, then drying the hydrocarbons by contact therewith of P2O5 of not greater impurity than that which has been previously used in the main purifying treatment infra, and which is effective to remove potential water-forming compds. detrimental to the action of the relatively fresh P2O5 in the treatment infra, passing a liquid stream of the so pretreated hydrocarbon to the lower part of a previously formed column thereof, adding a suspension in hydrocarbon liquid of relatively fresh P2O5 to the upper part of the column, decanting from adjacent to the top of the column a stream of the hydrocarbon laden with **P2O5**, slowing up the **flow** of such stream sufficiently to cause added P2O5 to settle, recovering in concd. **form** the **P2O5** in suspension thus settled out, and recovering the treated hydrocarbons.

CC 22 (Petroleum, Lubricants, and Asphalt)

=> d his l52-

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     FILE 'HCA' ENTERED AT 15:44:05 ON 10 AUG 2004
L52        66291 S HEXAG?
L53          269 S L4 AND L52
L54           22 S L53 AND L5-L8
L55            1 S L53 AND L9
L56            0 S L53 AND (L28 OR L29)
L57           20 S (L54 OR L55) NOT (L36 OR L51)
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=> d l57 1-20 cbib abs hitind

L57 ANSWER 1 OF 20 HCA COPYRIGHT 2004 ACS on STN

125:180102 Infrared reflectance spectra and formalism of precipitation of acicular magnetic particles in network glasses. Ram, S.; Ram, K. (Institute of Metal Research, Technical University of Berlin, Berlin, D-10623, Germany). Infrared Physics & Technology, 37(4), 457-469 (English) 1996. CODEN: IPTEEY. ISSN: 1350-4495. Publisher: Elsevier.

AB 1-2 Mm thin platelets of borate or silicate glasses ppt. peculiarly isolated magnetic particles (of micrometer sizes) of **hexagonal** ferrites, spinel ferrites, or garnets at reaction temp. A small 0.5-3.0 mol % additive of Ag2O, Bi2O3 or **P2O5** in these glasses behaves as a strong catalyst in undercooling the melt (in the shape of the platelets) in a truly amorphous metastable glass state of locally ordered network of interconnected basis structural units. In a typical 35BaO-25Fe2O3-40B2O3 borate glass, for example, the ordered structure in the 1-2 mm thin platelets results in 15-52 cm-1 increase in the B-O stretching vibration frequencies over the usual values in the bulk. The surface tension σ (which is modified by the additives) of the glass-liq. facilitates the chem. ordering of planar configurations of interconnected (B3O4.5)n → ∞ boroxol rings 1 over other along the surface of the platelets. On isothermal annealing at 500-850°, the planar network configurations (α) nucleate planar α-β interfaces with solid aggregates (β) of the immiscible (at this temp.) Ba2+ and Fe3+ cations caused in the network in the thermal induced recrystn. process of BaFe12O19 **hexagonal** ferrite. The initial shape and size of the α-β interface depends (in addn. to the σ and the free-energy difference ΔGv between the 2 phases α and β) on the size and shape of the crystal (β) unit cell and the local structure of the glass. It therefore assumes an elongated shape in the elongated P63/mmc **hexagonal** crystal lattice (of crystallog. axial ratio c/a .apprx. 3.94) of BaFe12O19 ferrite. That ultimately grows and ppts. in BaFe12O19 single crystal in the presumed acicular shape (along the c-axis) over the network, following the **flow** of the heat released in the reaction along the planar interface, maintained by the strong surface tension σ, surface anisotropy (δ), and α-β wetting. The results are modeled and discussed using the B-O stretching or bending vibrations in the thin glass-platelets and the platelets milled (removing the rather long range at. ordering) into powder of particle size of 1 μm or lower.

CC 73-3 (Optical, Electron, and Mass Spectroscopy and Other Related Properties)
Section cross-reference(s): 57, 77

IT 1304-76-3, Bismuth oxide (Bi2O3), uses **1314-56-3**, Phosphorus oxide (**P2O5**), uses 20667-12-3, Silver oxide (Ag2O)

(IR reflectance spectra and formalism of pptn. of acicular magnetic particles in network glasses)

L57 ANSWER 2 OF 20 HCA COPYRIGHT 2004 ACS on STN
111:42331 Lithium-aluminum-phosphorus oxide molecular sieve compositions. Flanigen, Edith M.; Lesch, David A.; Lok, Brent M. T.; Patton, Robert L.; Wilson, Stephen T. (Union Carbide Corp., USA). U.S. US 4789535 A 19881206, 26 pp. Cont.-in-part of U.S. Ser. No. 599,811, abandoned. (English). CODEN: USXXAM. APPLICATION: US 1986-834921 19860228. PRIORITY: US 1984-599811 19840413.

AB The cryst. mol. sieves, having a 3-dimensional microporous framework structure of LiO2, AlO2, and PO2 tetrahedral units and having the general (anhyd.) formula mR:(LixAlyPz)O2 (R = ≥1 org. templating agents present in the intercryst. pore system; m = molar amt. of R per mol (LixAlyPz)O2 and has value 0 to .apprx.0.3; x,y,z = mol fraction of Li, Al, and P, resp.), are disclosed. The mol fractions are located within a (described) **hexagon** in a triangular Al-L-P diagram (d-spacings presented). The crystn. mechanism of these products is detd. by the addn. of ≥1 templating agents. To a mixt. of water 265.6 and hydrated Al oxide in the form of pseudo-boehmite phase comprising Al2O3 69.0 and H2O 31.0 wt.% were added 40% Et4NOH 46.0 and Pr3N 125.4 g, and the mixt. was **stirred** until homogeneous. To 100.9 g of this mixt. was added under stirring 0.6 g Li3PO4. This mixt. was heated at 150° in a sealed and lined container for 16 h. The product contained C 4.9, N 0.66, Li2O 0.71, Al2O3 34.4 and **P2O5** 44.7 wt.%, and had loss on ignition 20.4 wt.%, corresponding to the anhyd chem. compn. 0.04Et4NOH:(Li0.04Al0.50P0.47)O2. X-ray diffraction data are presented.

IC ICM C01B025-26
NCL 423306000
CC 49-4 (Industrial Inorganic Chemicals)

L57 ANSWER 3 OF 20 HCA COPYRIGHT 2004 ACS on STN
86:109502 Refining of steelmaking slag. Ando, Ryo; Miyashita, Yoshio; Koyama, Tatsuo; Kubodera, Shoji (Nippon Kokan K. K., Japan). Jpn. Kokai Tokkyo Koho JP 51121422 19761023 Showa, 6 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1975-47328 19750418.

AB Molten slag in an elec. furnace having a **hexagonal** horizontal cross section is mixed with solid reductant and component-adjusting agent and **stirred** with an impeller to improve the slag reaction. By the method Fe, Mn, and P ore recycled and a cement clinker-like slag is obtained. For example, 10-ton converter slag contg. CaO 50.80, SiO2 16.86, Al2O3 1.08, MgO and MnO 3.48 each, Fe 13.65, **P2O5** 2.20, and S 3.377% was treated with 0.6 ton powd. coke and 1 ton alumina in a furnace at 70 **rpm** with 300 kWh/ton to contain 56.40, 16.37, 11.14, 4.99,

0, 2.46, 0.30, and 0.25, resp., and to obtain 1.9-ton pig iron [61933-23-1] contg. C 5.27, Si 0.28, Mn 12.70, P 2.75, and S 0.003%.
IC C21B003-06
CC 54-2 (Extractive Metallurgy)

L57 ANSWER 4 OF 20 HCA COPYRIGHT 2004 ACS on STN
59:25216 Original Reference No. 59:4563c-e Viscous **flow** and melt allotropy of **phosphorus pentoxide.** Cormia, R. L.; Mackenzie, J. D.; Turnbull, D. (Gen. Elec. Res. Lab., Schenectady, NY). Journal of Applied Physics, 34(8), 2245-8 (Unavailable) 1963. CODEN: JAPIAU. ISSN: 0021-8979.
AB The viscosity of liq. **P2O5** above and below the m.p. of the tetragonal crystal was detd. by the falling-sphere method. At the melting temp. of 580°, the viscosity is 5.15 + 106 P and the activation energy for viscous **flow** is 41.5 kcal./mol. These values suggest that, similar to liq. B2O3, or SiO2., the melt of tetragonal **P2O5** can be classified as a network liq. From qual. observations on m. behavior and a consideration of the ns of the cryst. and glassy phases, **hexagonal P2O5**, on the other hand, gives a mol. liq. on fusion. The "**hexagonal**" liq., however, is unstable and undergoes rapid polymn. to give the network liq.
CC 3 (General Physical Chemistry)
IT Activation energy
(of **flow**, of **P2O5**)
IT Polymerization
(of phosphorus oxide (**P2O5**))
IT **Flow**
(of phosphorus oxide (**P2O5**) melts)
IT **1314-56-3**, Phosphorus oxide, **P2O5**
(molten, allotropy and **flow** of)

L57 ANSWER 5 OF 20 HCA COPYRIGHT 2004 ACS on STN
57:3902 Original Reference No. 57:759e-i Heterocyclic compounds of nitrogen. IV. A synthesis of 3-iodo-2-(o-iodophenyl)indole. Bruce, J. Malcolm (Univ. Manchester, UK). Journal of the Chemical Society, Abstracts 1514-15 (Unavailable) 1962. CODEN: JCSAAZ. ISSN: 0590-9791. OTHER SOURCES: CASREACT 57:3902.
AB cf. CA 54, 9883b. o-IC6H4COCl treated with diethyl ethoxymagnesiomalonate and the mixt. hydrolyzed gave 84% o-ICr6H4Ac (I), b0.05 85-6°; 2,4-dinitrophenylhydrazone, orange **hexagonal** plates, m. 187.5° (BuOH); semicarbazone, **hexagonal** plates, m. 181-1.5° (EtOH). I (1.28 g.), 0.54 g. PhNHNH2, 1.5 g. 88-90% H3PO4, and 1 g. **P2O5** were **stirred** at 110°, the reaction allowed to subside, and the temp. raised to 150°, when an exothermic reaction occurred; the mixt. heated 2 min. at 180°, cooled, dild. with 12 ml. water, extd. with ether, washed, dried, the solvent removed,

and the residue distd. gave 0.12 g. I and 27% 2-(Oiodophenyl)indole (II), orange-yellow viscous oil; 1,3,5trinitrobenzene adduct, deep red needles, m. 115.5-16° (C6H6-ligroine). Alternately, 4.82 g. I and 2.16 g. PhNH- NH2 were heated 30 min. at 150°, then 30 min. at 100°/30 mm.; 30 g. powd. anhyd. ZnCl2 was added, the mixt. **stirred** 15 min. at 180°, cooled, and digested on a water bath with 50 ml. 2% HCl until no further material dissolved; extn. with C6H6 was followed by washing with HCl, water, and drying; the soln. was concd. to 25 ml., chromategraphed on Al2O3, duted with C6H6 until it was no longer yellow, and the solvent removed and distd. to give 57% II. II (3.61 g.) in 15 ml. C5H5N at 0° was treated 115 min. with 1.98 g. ICl in 15 ml. dioxane, and kept 60 hrs. at 0° the solvent was removed at 25 mm., the residue dild. with water, extd. with ether, washed with water, dried, and evapd.; the residue in 10 ml. C6H6 was chromatographed on Al2O3 and eluted with C6H6 until colorless. Removal of solvent and crystn. from 30 ml. cyclohexane gave 76% 3-iodo-2-(Oiodophenyl)indole (III), m. 124.5-5°; 1,3,5-trinitrobenzene adduct, orange-red laths, m. 141° (C6H6-tigroine). III heated with Cu2O gave II; III similarly heated with Cu2O, prepd. by redn. of Cu(OAc)2 with N2H4, gave 2-phenylindole, m. 189.5-90°.

CC 31 (Heterocyclic Compounds-One Hetero Atom)

L57 ANSWER 6 OF 20 HCA COPYRIGHT 2004 ACS on STN

54:118062 Original Reference No. 54:22507e-i,22508a-i,22509a-i,22510a-g Elimination of nonangular alkyl groups in aromatization reactions. IV. Cocker, Wesley; Hopkins, L. O.; Mabrouk, L.; McCormick, J.; McMurry, T. B. H. (Trinity Coll., Dublin, Ire.). Journal of the Chemical Society, Abstracts 2230-42 (Unavailable) 1960. CODEN: JCSAAZ. ISSN: 0590-9791.

AB cf. CA 49, 8891e. New di-, tri-, and tetraalkylnaphthalenes were synthesized, including 2 completely substituted in the peri positions. Their infrared spectra were recorded. Spectroscopic characteristics of the last 2 compds. showed no abnormalities which could arise from overlap of the alkyl groups. Two cases of the loss of Et group during dehydrogenation with Se and with Pd-C were reported. β-Benzoyl-α-methylpropionic acid (38 g.) with CH2N2 in MeOH-Et2O gave 37 g. Me β-benzoyl-α-methylpropionate (I), prisms, m. 56°. EtMgI (from 39 g. EtI, 6 g. Mg, and 86 cc. Et2O) added slowly to 5 g. I in 20 cc. Et2O, the mixt. refluxed 1 hr. , set aside overnight, and the complex decompd. gave 0.5 g. Me 2-methyl-4-phenyl-3-hexenoate (II), b17 165°, n20D 1.5194, λ 243.5 mμ, log ε 3.24, ν 1770 cm.-1 I (20.6 g.) in 100 cc. Et2O added dropwise to 0.138 mole EtMgI in 50 cc. Et2O at 0°, after 0.5 hr. the mixt. allowed to warm to room temp., 30 cc. PhMe added, the Et2O removed, the residue heated 6 hrs. at 100°, and worked up as usual gave 16 g. II;

S-benzylisothiuronium salt m. 126°. II (15 g.) in 60 cc. MeOH with 1 g. Raney Ni at 100°/70 atm. H gave 12.4 g. 2-methyl-4-phenylhexanoic acid (III), b17 183°, ν 1706 cm.-1 III (12.4 g.) added to cold polyphosphoric acid (from 33.4 cc. 90% H3PO4 and 35.3 g. **P2O5**) in 1 hr. at 165°, the mixt. heated 5 min. at 165°, cooled, poured into cold H2O, and extd. with Et2O gave 8.5 g. 4-ethyl-1,2,3,4-tetrahydro-2-methyl-1-oxonaphthalene (IV), b1 101°, ν 1691 cm.-1 IV (3 g.), 60 cc. PhMe, 5 cc. AcOH, 200 cc. HCl, 45 cc. H2O, and 80 g. Zn-Hg refluxed 60 hrs. gave 1 g. 4-ethyl-1,2,3,4-tetrahydro-2-methylnaphthalene (V), b1 71°. V (0.9 g.) heated 4 hrs. at 260-80° with 0.9 g. Pd-C, the product collected in Et2O, and distd. gave 0.2 g. 1-ethyl-3-methylnaphthalene, b22 140°, n24D 1.5969; picrate, brick-red needles, m. 112.5° (MeOH); trinitrobenzene adduct m. 115° (MeOH); styphnate, yellow needles, m. 119.5° (AcOH); trinitrotoluene adduct m. 75°(MeOH). α-Bromopropiophenone (45.5 g.) heated 6 hrs. with 6 g. Na and 45.5 g. Et malonate in 200 cc. C6H6 and the ester hydrolyzed with excess MeOH-KOH gave 15 g. 1-benzoylethylmalonic acid (VI), m. 158°. VI heated at 160° until effervescence ceased gave 5.5 g. β-benzoylbutyric acid (VII), prisms, m. 58° (H2O). VII (5.5 g.) refluxed 40 hrs. with 20 cc. concd. HCl, 9 cc. H2O, 12 cc. PhMe, and 16 g. Zn-Hg gave 3.5 g. β-methyl-γ-phenylbutyric acid (VIII), b15 172°, ν 1716, 1794 cm.-1 VIII (2.4 g.) heated 10 min. at 90° with 16 cc. concd. H2SO4, poured on H2O, and extd. with Et2O gave 1 g. 1,2,3,4-tetrahydro-3-methyl-1-oxonaphthalene (IX), b14 128°. IX (0.9 g.) in 20 cc. Et2O refluxed 3 hrs. with EtMgI (from 5 cc. EtI) and the complex decompd. gave 0.6 g. 1-ethyl-3,4-dihydro-3-methylnaphthalene, b14 136°. EtHC(CO2Et)2 (188 g.) added slowly to NaOEt (from 23 g. Na), the mixt. cooled, 1 g. NaI added followed by dropwise addn. of 122.5 g. ClCH2CO2Et, the mixt. refluxed 20 hrs., the alc. removed, the residue dild. with H2O, and extd. with Et2O gave 150 g. tri-Et butane-1,2,2-tricarboxylate (X), b60 193°. X refluxed with excess concd. HCl gave 60 g. ethylsuccinic acid (XI), m. 97° (C6H6-Et2O). XI (60 g.) distd. and then redistd. gave 45 g. ethylsuccinic anhydride (XII), b25 146°. AlCl3 (180 g.) added to 74 g. XII in 65 cc. C6H6 and 225 cc. CH2Cl2 and the mixt. **stirred** 18 hrs. gave 78 g. β-benzoyl-α-ethylpropionic acid, m. 85° (ligroine); Me ester (XIII) b1 132°, ν 1730 and 1685 cm.-1. BzH (1.06 g.) in 15 cc. MeOH heated 10 min. at 40° with 1 g. XIII and 0.54 g. NaOMe in 5 cc. MeOH, the mixt. set aside overnight, the MeOH removed, the residue acidified, and extd. with Et2O gave 1.5 g. 3-benzoyl-2-ethyl-4-phenyl-3-butenoic acid, m. 123° (ligroine), ν 1702, 1651, 1600 cm.-1 XIII (30 g.) and MeMgI (from 27.43 g. MeI) gave 19 g. 2-ethyl-4-phenylpent-3-enoic acid (XIV), b1

135°, m. 50-1°, ν 1700 cm.-1 XIV (32 g.) hydrogenated over Raney Ni in MeOH at 100°/80 atm. gave Me ester, hydrolyzed with 7.5% MeOH-KOH to 17 g. α-ethyl-γ-phenylvaleric acid (XV), b1 139°, ν 1700 cm.-1 Cyclization of 17 g. XV with polyphosphoric acid gave 9 g. 2-ethyl-1,2,3,4-tetrahydro-4-methyl-1-oxonaphthalene (XVI), b1 123°, λ 248 and 289 mμ, log ε 4.98 and 4.16, ν 1680 cm.-1 XVI (3 g.) reduced as above gave 1 g. 3-ethyl-1,2,3,4-tetrahydro-1-methylnaphthalene (XVII), b1 77°. XVII (0.6 g.) heated 4.5 hrs. at 260-70° with 0.6 g. Pd-C and the product extd. with C6H6 gave 3-ethyl-1-methylnaphthalene, oil; picrate, orange needles, m. 83° (MeOH). β-(p-Ethylbenzoyl)propionic acid (30 g.) refluxed 2 hrs. with 50 cc. MeOH and 5 cc. concd. H2SO4 gave 28.8 g. Me ester (XVIII), b1 134°, m. 33°, ν 1754 cm.-1 EtMgI (from 30.2 g. EtI) in 60 cc. Et2O treated with 28.8 g. XVIII in 100 cc. Et2O gave 12.5 g. 4-(p-ethylphenyl)-3-hexenoic acid (XIX), oil, b1 182°, ν 1715 cm.-1 XIX (12.5 g.) in 100 cc. MeOH hydrogenated over Raney Ni at 100°/110 atm. gave a mixt. of satd. acid and ester, which refluxed 2 hrs. with 50 cc. 5% MeOH-KOH gave 5.5 g. 4-(p-ethylphenyl)hexanoic acid (XX), b1 132-3°, ν 1700 cm.-1 XX (12 g.) cyclized with polyphosphoric acid 3 min. at 165° gave 9 g. 1,6-diethyl-1,2,3,4-tetrahydro-4-oxonaphthalene (XXI), b1 117-18°, ν 1680 cm.-1 XXI (3.3 g.) in 60 cc. PhMe refluxed 42 hrs. at 260-80° with 80 g. Zn-Hg, 100 cc. concd. HCl, and 5 cc. AcOH in 45 cc. H2O gave 1.2 g. 1,6-diethyl-1,2,3,4-tetrahydronaphthalene (XXII), b1 92°. XXII (1 g.) heated 4 hrs. at 260-80° with 1 g. Pd-C gave 0.8 g. 1,6-diethylnaphthalene, b1 76°, n21D 1.5806; picrate m. 70° (MeOH). 7-Ethyl-1,2,3,4-tetrahydro-1-oxonaphthalene (7.7 g.) in 25 cc. Et2O refluxed 3 hrs. with EtMgI (from 12.3 g. EtI), the product set aside 2 hrs. with 20 cc. anhyd. HCO2H, poured into H2O, and extd. with Et2O gave 5.7 g. 1,7-diethyl-3,4-dihydronaphthalene (XXIII), b1 79°. Dehydrogenation of 3 g. XXIII with Pd-C 4 hrs. at 260-70° gave 2.5 g. 1,7-diethylnaphthalene, b1 87°, n20D 1.5858; picrate, orange needles, m. 78°. XVI (1 g.) in 10 cc. Et2O refluxed 7 hrs. with MeMgI (from 3.5 g. MeI), left overnight, and the complex decompd. gave 0.6 g. 3-ethyl-1,2-dihydro-1,4-dimethylnaphthalene (XXIV), b1 75°. XXIV (0.4 g.) heated 4.5 hrs. at 260-80° with Pd-C gave 2-ethyl-1,4-dimethylnaphthalene, oil; trinitrobenzene adduct, yellow needles, m. 123° (MeOH). IV (2.5 g.) in 10 cc. Et2O refluxed 2 hrs. with MeMgI (from 3.8 g. MeI) and decompd. with ice and NH4Cl gave 4-ethyl-1,2,3,4-tetrahydro-1-hydroxy-1,2-dimethylnaphthalene (XXV), **hexagonal** prisms, m. 73° (ligroine). XXV set aside 2 hrs. with 10 cc. anhyd. HCO2H gave 1-ethyl-1,2-dihydro-3,4-dimethylnaphthalene (XXVI), b1

150°. XXVI (1.3 g.) heated 4 hrs. at 260-80° with 1.3 g. Pd-C and the product extd. with MeOH gave 0.8 g. 4-ethyl-1,2-dimethylnaphthalene, b1 136°, n23D 1.6021; picrate, orange needles, m. 117° (MeOH); trinitrobenzene adduct, golden needles, m. 118° (MeOH); styphnate, orange needles, m. 119° (AcOH). I (14 g.) in 75 cc. Et2O refluxed 3 hrs. with MeMgI (from 13.3 g. MeI), set aside 18 hrs., the complex decompd., the mixt. extd. with Et2O, and the ext. washed with 5% Na2CO3 gave 3 g. 2-methyl-4-phenyl-3-pentenoic acid (XXVII), b1 150°, ν 1712 cm.-1 The ether ext. afforded 6.5 g. neutral oil, b1 118°, ν 1778 cm.-1 Hydrolysis of the oil 3 hrs. with 36 cc. 5% MeOH-KOH gave 5 g. XXVII. XXVII (12 g.) in 50 cc. MeOH hydrogenated over Raney Ni at 10°/70 atm. gave the satd. ester. Hydrolysis of the ester 2 hrs. with 100 cc. 5% MeOH-KOH gave 10 g. α-methyl-γ-phenylvaleric acid (XXVIII), b1 125°,ν 1713 cm.-1 XXVIII (4.8 g.) heated 3 min. at 165° with polyphosphoric acid gave 2.6 g. 1,2,3,4-tetrahydro-2,4-dimethyl-1-oxonaphthalene (XXIX), b1 88-9°,ν 1694 cm.-1 XXIX (1.4 g.) in 10 cc. Et2O refluxed 3 hrs. with EtMgI (from 3.8 g. EtI), the complex decompd., and extd. with Et2O gave 0.9 g. 4-ethyl-1,2-dihydro-4-hydroxy-1,3-dimethylnaphthalene (XXX), **hexagonal** prisms, m. 85° (ligroine). XXX set aside 2 hrs. with 10 cc. anhyd. HCO2H gave 0.7 g. 4-ethyl-1,2-dihydro-1,3-dimethylnaphthalene (XXXI), b1 95°. XXXI (0.6 g.) heated 3 hrs. at 260-80° with 0.6 g. Pd-C and the mixt. extd. with C6H6 gave 1 g. 1-ethyl-2,4-dimethylnaphthalene, b2 109°, n23D 1.5975; picrate m. 94° (MeOH). Me β-(p-toluoyl)propionate (41 g.) in 100 ml. Et2O treated with EtMgI (from 43 g. EtI) gave 15 g. 4-(p-tolyl)-3-hexenoic acid (XXXII), b1 137-41°,ν 1710 cm.-1 XXXII (20 g.) hydrogenated in 75 cc. MeOH over 2 g. Raney Ni at 100°/80 atm. gave 20 g. Me 4-(p-tolyl)hexanoate (XXXIII), b1 99°,ν 1740 cm.-1 Hydrolysis of XXXIII with 120 cc. 5% MeOH-KOH gave 17 g. 4-(p-tolyl)hexanoic acid (XXXIV), b1 155°, m. 36°. XXXIV (16 g.) heated 5 min. at 165° with polyphosphoric acid and the mixt. extd. with Et2O gave 15 g. 4-ethyl-1,2,3,4-tetrahydro-7-methyl-1-oxonaphthalene (XXXV), b2 134°, λ 254 and 295 mμ, log ε 4.21 and 3.74,ν 1683 cm.-1; semicarbazone, rhombs, m. 165-6° (dil. alc.). XXXV (5 g.) in 25 cc. Et2O refluxed 3.5 hrs. with MeMgI soln. gave 3 g. 1-ethyl-1,2-dihydro-4,6-dimethylnaphthalene (XXXVI), b1 115°. XXXVI (2 g.) heated 4 hrs. at 260-80° with 2 g. Pd-C and the product extd. with C6H6 gave 1.3 g. 1-ethyl-4,6-dimethylnaphthalene, b1 85°; picrate, orange needles, m. 85° (MeOH); trinitrobenzene adduct, yellow needles, m. 109° (MeOH). IV (2.9 g.) in 15 cc. Et2O refluxed 4 hrs. with EtMgI soln. and the product set aside 2 hrs. in 10 cc. anhyd. HCO2H, dild. with H2O, and extd. with Et2O

gave 1.5 g. 1,4-diethyl-1,2-dihydro-3-methylnaphthalene (XXXVII), b1 140°. XXXVII (9.4 g.) heated 4 hrs. with 1.4 g. Pd-C at 260-80° gave 0.8 g. 1,4-diethyl-2-methylnaphthalene, b1 142°, n21D 1.5935; picrate, orange-red needles, m. 62° (MeOH); trinitrobenzene adduct m. 97° (MeOH); trinitrotoluene adduct, yellow needles, m. 68° (MeOH). XXXV (5 g.) in 25 cc. Et2O refluxed 4 hrs. with EtMgI soln. gave 2.7 g. dihydro compd., b2 123°. The dihydro compd. (2 g.) heated 4 hrs. at 260-80° with 2 g. Pd-C gave 1.2 g. 1,4-diethyl-6-methylnaphthalene, b1 112°; picrate m. 71-2° (MeOH); trinitrobenzene adduct m. 101°. XXI (3.3 g.) in 10 cc. Et2O refluxed 2 hrs. with MeMgI (from 2 cc. MeI) and set aside 2 hrs. with 12 cc. HCO2H gave 3 g. 1,6-diethyl-1,2-dihydro-4-methylnaphthalene (XXXVIII), b1 89°. XXXVIII (1.4 g.) heated 4 hrs. at 260-80° with 1.4 g. Pd-C gave 1.1 g. 1,6-diethyl-4-methylnaphthalene, b1 90°, n21D 1.5859; picrate m. 56°; trinitrobenzene adduct m. 80° (MeOH). XVIII (84.4 g.) in 250 cc. Et2O refluxed 5 hrs. with MeMgI (from 75.2 g. MeI) gave 6.5 g. 4-(p-ethylphenyl)-3-pentenoic acid (XXXIX), b1 138°,ν 1719 cm.-1 Crude XXXIX (10 g.) hydrogenated 6 hrs. in 50 cc. MeOH over 1 g. Raney Ni at 100°/110 atm. and hydrolyzed with 100 cc. 5% MeOH-KOH gave 9.5 g. γ-(p-ethylphenyl)valeric acid (XL), b1 137°,ν 1706 cm.-1 XL (6 g.) cyclized with polyphosphoric acid gave 4.5 g. 6-ethyl-1,2,3,4-tetrahydro-1-methyl-4-oxonaphthalene (XLI), b1 113°,ν 1682 cm.-1 XLI (2.5 g.) in 15 cc. Et2O refluxed 4 hrs. with EtMgI (from 6.7 g. EtI) and the product set aside 2 hrs. in 10 cc. anhyd. HCO2H gave 1.6 g. 4,6-diethyl-1,2-dihydro-1-methylnaphthalene (XLII), b1 96°. XLII (1.2 g.) heated 4 hrs. at 260-70° with 1.2 g. Pd-C gave 0.9 g. 4,6-diethyl-1-methylnaphthalene, b. 110°, n25D 1.5808; picrate m. 76.5°. XXI (4 g.) in 12 cc. Et2O refluxed 2 hrs. with EtMgI and the product set aside 2 hrs. in 10 cc. anhyd. HCO2H gave 3.1 g. 1,4,6-triethyl-1,2-dihydronaphthalene (XLIII), b1 119°. XLIII (2.9 g.) heated 4 hrs. at 260-80° with 2.9 g. Pd-C gave 2 g. 1,4,6-triethylnaphthalene, b3 128°, n25D 1.5770; picrate m. 53°. Me β-(2,5-dimethylbenzoyl)propionate (XLIV) (21 g.) was obtained as an oil, b1 148°, n19D 1.5202,ν 1754 cm.-1, when the corresponding acid (30 g.) was refluxed 2 hrs. with MeOH-H2SO4. XLIV (15 g.) in 20 cc. Et2O treated 18 hrs. with EtMgI gave 5 g. 4-(2,5-dlmethylphenyl)hex-3-enoic acid (XLV), b1 146°, ν 1715 cm.-1, along with recovered XLIV. XLV (30 g.) hydrogenated in 80 cc. MeOH over 2 g. Raney Ni at 100°/120 atm. gave 32 g. Me 4-(2,5-dimethylphenyl)hexanoate (XLVI), b1 133°, 1745 cm.-1; XLVI refluxed 6 hrs. with 160 cc. 5% MeOH-KOH gave 22.5 g. 4-(2,5-dimethylphenyl)hexanoic acid (XLVII), b1 149°, 1715 cm.-1 XLVII (12.4 g.) heated 5 min. at 165° with

polyphosphoric acid gave 7.8 g. 1-ethyl-1,2,3,4-tetrahydro-5,8-dimethyl-4-oxonaphthalene (XLVIII), b1 121°,ν 1675 cm.-1 XLVIII (3 g.) in 15 cc. Et2O refluxed 14 hrs. with MeMgI (from 4.2 g. MeI) gave 0.4 g. 1-ethyl-1,2-dihydro-4,5,8-trimethylnaphthalene (XLIX), b1 120°. XLIX (0.4 g.) heated 3 hrs. with 0.4 g. Pd-C gave 0.2 g. 1-ethyl-4,5,8-trimethylnaphthalene, b3 118°, n19D 1.5841; picrate, brick-red needles, m. 110° (MeOH). XLVIII (5 g.) in 25 cc. Et2O with EtMgI gave a product which set aside 2 hrs. in 20 cc. HCO2H gave 1.7 g. 1,4-diethyl-1,2-dihydro-5,8-dimethylnaphthalene (L), b1 101°. L (1.3 g.) heated 4 hrs. at 260-80° with 1.3 g. Pd-C gave 1 g. 1,4-diethyl-5,8-dimethylnaphthalene, b1 107°, n20D 1.5844; picrate m. 135° (MeOH). β-(o-Methoxyphenyl)butyric acid (25 g.) refluxed 1 hr. with 20 cc. SOCl2 gave 24.7 g. β-(o-methoxyphenyl)butyryl chloride (LI), b3 144-5°. LI (26.1 g.) in 150 cc. Et2O slowly added to 12.1 g. CH2N2 in 700 cc. Et2O, the mixt. set aside 2 days, the solvent removed, the residue dissolved in 257 cc. dioxane at 50°, heated 2 hrs. with a mixt. of 150 cc. 30% NH4OH and 40 cc. 10% AgNO3, filtered, the solvents evapd., and the residue triturated with ligroine gave 16.2 g. γ-(o-methoxyphenyl)valeramide (LII), m. 76° (C6H6). LII (16.2 g.) refluxed 5 hrs. with 100 cc. 15% aq. KOH, the mixt. acidified, and extd. with Et2O gave 16 g. γ-(o-methoxyphenyl)valeric acid (LIII), prisms, m. 66-7° (ligroine). LIII (15 g.) heated 5 min. at 165° with polyphosphoric acid, cooled, poured on ice, extd. with Et2O, and evapd. gave 4.1 g. solid, C12H14O2, m. 242° (EtOAc). The oil from the filtrate distd. gave 5.5 g. 1,2,3,4-tetrahydro-5-methoxy-4-methyl-1-oxonaphthalene (LIV), b1 107°, ν 1686 cm.-1 LIV (5.5 g.) reduced 30 hrs. with 69 g. Zn-Hg in 69 cc. concd. HCl, 42 cc. H2O, 1.5 cc. AcOH, and 20 cc. PhMe gave 3.3 g. 1,2,3,4-tetrahydro-5-methoxy-4-methylnaphthalene (LV), b. 78°. LV (3.4 g.) heated 4 hrs. at 260-80° with 3.4 g. Pd-C gave 2.1 g. 1-methylnaphthalene, b1 60° (picrate m. 143°), and 0.1 g. 1-methoxy-8-methylnaphthalene (LVI), b1 98° (picrate m. 154°). LV (2.2 g.) heated 3 hrs. with 0.4 g. S at 220-30° gave 1.2 g. LVI, n26D 1.5625, λ 229, 280, 292, and 326 mμ, log ε 4.48, 3.54, 3.55, and 2.98. LVI refluxed 2 hrs. with 30 cc. HI and 33 cc. AcOH, cooled, dild., extd. with Et2O, the ext. washed and treated with 10% NaOH, the alk. ext. acidified, and extd. with Et2O gave 0.3 g. naphthol, b4 110°; picrate m. 190° (MeOH).

CC 10F (Organic Chemistry: Condensed Carbocyclic Compounds)

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52:40407 Original Reference No. 52:7214c-i,7215a-f Natural tannins. XXVIII. Synthesis of 1,3,6-trigalloylglucose. Schmidt, Otto Th.; Klinger, Gunther (Univ. Heidelberg, Germany). Ann., 609, 199-208

(Unavailable) 1957.

AB All evapns. were carried out in vacuo. Soly. data for all new compds. are given. Unless otherwise stated, compds. were dried over **P2O5** at 40-80°/0.3-2 mm. Triacetyllevoglucosan (15 g.) was benzylated by Zemplen's method (cf. Z., et al., C.A. 31, 85141); the crude product in 50 cc. Pr2O was dried with Na2SO4 and filtered, giving 20% 2,4-dibenzyllevoglucosan (I), needles or leaflets, m. 106.5-107° (EtOH), [α]20D -28.5° (c 3.4, CHCl3). 2,4-Dibenzylglucose (II) (prepd. by Z.'s method, loc. cit.), recrystd. from aq. dioxane, Me2CO, or EtOH and air-dried formed II.0.5H2O, m. 100-3° (by preheating the block to 95°), [α]20D 32.4 ± 0.5° (c 5, EtOH). (Z. gives 75-9°, and [α]20D 25.1°). Under carefully controlled, fully described conditions anhyd. cryst. II, m. 117-20°, [α]20D 35 ± 0.8° (c 3.5, EtOH), was obtained. Neither form of II shows mutarotation. Anhyd. II (1.5 g.) and 9 g. tribenzylgalloyl chloride (IIa) in 50 cc. purified dry CHCl3 and 2.5 cc. quinoline, kept 2 days at 40°, and 6 days at 60°, dild. with 200 cc. CHCl3 and washed successively with 2N H2SO4, dil. NaHCO3 and H2O, dried, evapd., dissolved in 40 cc. C6H6, kept 24 hrs. with sepn. of 2.4 g. tribenzylgallic acid (III). The C6H6 mother liquor was chromatographed on Woelm neutral Al2O3 (IIIa), eluted with C6H6; the sirup from the evapd. eluate in 15 cc. AcOEt at 0° gave 2.1 g. tribenzylgallic anhydride (IV), m. 166°, the evapd. mother liquor from which yielded small amts. of IV and 0.1 g. 1,6(?)-bis(tribenzylgalloyl)-2,4-dibenzylglucose (V), m. 104° (AcOMe), [α]20D 28° (c 2, AcOEt). To 34.88 g. III in dry dioxane and 13.84 g. AgNO3 in 100 cc. H2O and 150 cc. MeOH were added 23 cc. 6% NH3 in MeOH, giving, after 24 hrs. at 0°, 34 g. Ag salt (VI) of III, decomp. 245°, difficultly sol. or insol. in neutral solvents, sol. in dioxane contg. acid or NH3; quite stable to light, but not direct sunlight. Acetobromoglucose (2.55 g.) and 3.42 g. powd. VI, suspended and shaken in 70 cc. PhMe was refluxed 4 min., cooled, filtered, and passed through IIIa which was then washed with 50 cc. C6H6. The filtrate and washings, evapd. gave 3.2 g. 1-(tribenzylgalloyl)-2,3,4,6-tetraacetyl-β-D-glucose, m. 150° (BuOH), [α]20D -24.7° (c 4, AcOEt), 2.13 g. of which, hydrogenated in 20 cc. abs. MeOH and 40 cc. AcOEt, with 0.06 g. Pd gave 1-galloyl-2,3,4,6-tetraacetyl-β-D-glucose (VII), cubes or thick needles, m. 200° (aq. MeOH), [α]20D -47° (c 2, MeOH), which was deacetylated at 20° with MeONa in abs. EtOH, giving glucogallin, m. 216-18°. VIII with Ac2O and pyridine gave heptaacetylglucogallin, m. 125-6°, [α]20D -24° [(CHCl2)2]. I (10.3 g.) and 16.5 g. IIa in 50 cc. pyridine kept 8 days at 40°, poured into 0.5 l. H2O and **stirred** intermittently during 24 hrs., gave a ppt. which, after washing with H2O was dried over H2SO4. This mixt. in 180 cc.

warm C_6H_6 was kept 24 hrs. at 20° and filtered, and the filtrate dild. with 180 cc. C_6H_6, passed through IIIa, evapd. to dryness, and dissolved in boiling iso-Pr_2O giving 17.6 g. (crude) 3-(tribenzylgalloyl)deriv. (VIII) of I, $C_{48}H_{44}O_9$, m. 90° (MeOH or iso-Pr_2O), [α]20D -31° (c 2, AcOEt). VIII (3.05 g.) in 30 cc. AcOEt and 20 cc. MeOH, hydrogenated with 0.06 h. Pd gave 3-galloyllevoglucosan, **hexagons**, m. 250° (without decompn.) (H_2O), [α]20D -49.5° (c 2, abs. MeOH); pentaacetate, m. 150° (MeOH), [α]20D -34.2° (c 2, $CHCl_3$). To VIII (4 g.) in 91 cc. C_6H_6 was added 16.8 gg. $(CF_3CO)_2O$ followed by the dropwise addn. of 2.8 cc. of a soln. (VIIIa) prepd. at 0° by adding 1 cc. H_2SO_4 to 10 cc. anhyd. dioxane. The mixt. kept sealed 24 hrs. at 20°, was poured into ice-H_2O and extd. with a mixt. of 120 cc. AcOEt and 200 cc. Et_2O; the org. phase washed 8 times with 90 cc. each of a satd. $NaHCO_3$ soln. and twice with satd. Na_2SO_4, dried over Na_2SO_4, decolorized with little C, evapd. to dryness, refluxed 1-1.5 hrs. with MeOH, evapd., dried over **P_2O_5**, taken up in 100 cc. AcOEt, and chromatographed on IIIa, yielded unchanged VIII in the 1st 300 cc. (AcOEt) eluate. The following 200 cc. AcOEt combined with a succeeding 250 cc. of a 9:1 AcOEt-MeOH mixt. was decolorized with Carboraffin, evapd., dissolved in 25 cc. AcOEt and treated cautiously with petr. ether (so as not to effect a permanent cloudiness) yielded 1.5 g. anhyd. 2,4-dibenzyl-3-(tribenzylgalloyl)glucose (IX), m. 115°, [α]20D 6.7 ± 1° (c 2.1, MeOH). A soln. of IX in MeOH evapd. and allowed to crystallize gave IX.-$3H_2O$ (IXa) (recrystd. from aq. MeOH or Me_2CO), [α]20D 5.7 ± 1° (c 2.1, MeOH). IXa on a block preheated to 90°, melted instantly. IXa heated gradually softened 90-95°, m. 112°. Dry IX (1.53 g.) and 2.14 g. IIa in 7.6 cc. pyridine were kept 50 days at 60°, evapd., dried over H_2SO_4, dissolved in 50 cc. C_6H_6, washed with aq. $NaHCO_3$ and H_2O, dried, concd. to 25 cc., seeded with III, kept 24 hrs. at 20°, filtered, dild. with 40 cc. C_6H_6 and chromatographed on IIIa to give 320 mg. 1,3,6-tris(tribenzylgalloyl)-2,4-dibenzylglucose (X), $C_{104}H_{90}O_{18}$, microneedles, m. 144° (AcOEt), [α]20D 24.2 ± 0.5° (c 2, AcOEt). X (0.65 g.) hydrogenated in 90 cc. AcOEt and 30 cc. MeOH, with 0.3 g. Pd gave 250 mg. foam, which in 4 cc. 50% Me_2CO was treated with C, and freed from Me_2CO, giving 1,3,6-trigalloyl-β-D-glucose, [α]20D 29.5 ± 1.5° (c 2.2, abs. EtOH), Rf 0.38, identical with the natural product described in the preceding part. VIII (2.34 g.) in 53 cc. C_6H_6 with 2.53 g. dry III was treated with 11 cc. $(CF_3CO)_2O$ and 1.64 cc. soln. VIIIa, kept 24 hrs. at 20°, poured into ice-H_2O, and extd. with 1:2 AcOEt-Et_2O. The washed and dried org. phase, decolorized with C, was evapd., taken up in 100 cc. C_6H_6, kept 24 hrs. (thus freed from most III), filtered, evapd., refluxed 1 hr. with 20 cc. MeOH, evapd. dissolved

in 50 cc. C6H6, and chromatographed on IIIa, give 0.5 g. 2,4-dibenzyl-3,6-bis(tribenzylgalloyl)glucose, m. 132-4°, [α]20D 29° (c 2, AcOEt), showing no mutarotation, giving, on paper a reddish-brown coloration with PhNH2 acid phthalate. The significance of the various reactions, in terms of the configuration of the compds. is discussed.

CC 10 (Organic Chemistry)

L57 ANSWER 8 OF 20 HCA COPYRIGHT 2004 ACS on STN

51:66529 Original Reference No. 51:12040i,12041a-i,12042a-g Natural tannins. XXIV. Synthesis of octamethylvaloneaic acid. Schmidt, Otto Th.; Komarek, Ernst; Rentel, Heinz (Univ. Heidelberg, Germany). Ann., 602, 50-60 (Unavailable) 1957.

AB cf. C.A. 50, 2487h. All m.ps. were taken with the Bock Monoscope app. and were cor. Most compds. were dried over **P2O5** at 0.4 mm. and appropriate temps. Chromatograms were made on Schleicher and Schull papers rendered hydrophobic by immersion in 3 or 10% silicone oil (AK 1000, Wacker-Chemie) dissolved in cyclohexane, and dried in air; those areas of the papers that were to be immersed in the solvent trough were left untreated. The chromatographic tanks were kept satd. with CHCl3 vapor before the CHCl3-satd. solvent (consisting of H2O contg. 2% AcOH and 1% MeOH) was introduced into the trough. Chromatograms were run at 10°, and after drying were developed either by spraying with 2-HO2SC6H4N2Cl (when free phenolic OH groups were present) or else treated 3 min. with Br vapor and 20 min. with NH3 and then viewed under ultraviolet (U.V.) light. Extensive (qual.) soly. data are given. Tetraacetylellagic acid (I) (12 g.) and 20 g. recently ignited K2CO3 in pure BzMe was **stirred** 6 hrs. at 125-30°, cooled, filtered, washed with a little MeOH, suspended in 400 cc. H2O, and acidified with 18% HCl; the ppt. washed with H2O, MeOH, and Et2O gave 6 g. 4,4'-diacetylellagic acid (II), prisms, not m. at 350°. II gave no color with FeCl3, and responded negatively to the Griessmayer-Reichel (G.-R.) reaction for ellagic acid. The 3,3'-di-Me deriv. (III) of II, prisms, m. 302-5° (from HCONMe2 or dioxane). Sapon. of 5 g. III by refluxing 2 hrs. with 2N KOH in MeOH (preferably under H) followed by diln. with H2O and acidification with 2N H2SO4 gave 3.2 g. 3,3'-dimethylellagic acid (IV), pale yellow, m. 319-20° (from HCONMe2 or dioxane), giving neither the FeCl3 nor the G.R. reaction. In hot dioxane IV gave reddish violet colorations with active PbO. Crude II (12 g.) was freed from part of the ellagic acid (V) by extg. with hot MeOH, methylated with CH2N2, and sapond. first with 2N KOH in MeOH and then with aq. N KOH, filtered, and the filtrate acidified with 18% HCl giving almost exclusively V, the filtrate from which was heated, giving 3.8 g. IV. To BzMe (400 cc.), 21 g. IV, and 60 g. dry K2CO3 **stirred** and heated at 140° was added 100 cc. PhCH2Cl in 10 portions every 30 min. More rapid

addn. caused losses in yield. After heating 2 hrs., the cooled product was washed with MeOH and H2O giving 27.3 g. 4,4'-dibenzyl deriv. (VI) of IV, **hexagons**, m. 295-6° (when preheated to 280°) (from BzMe or HCONMe2). To 5.2 g. VI in 50 cc. boiling 2N KOH in MeOH, H2O was added dropwise until the soln. was clear, MeOH was removed in vacuo, another 30 cc. H2O added, and the filtered mixt. at 0° acidified with HCl giving 4.1 g. 2,2'-dihydroxy-3,3'-dimethoxy-4,4'-dibenzyloxy-6,6'-dicarboxybiphenyl (VII), long needles, readily lactonized and showing no definite m.p. (from Me2CO by addn. of petr. ether); the 2,2'-di-MeO analog (VIII) of VII, prismatic rods, m. 236° (from MeOH), was formed by treating VI with aq. 2N NaOH, methylating with Me2SO4, pptg. with HCl, and sapong. any residual ester with KOH in MeOH. The di-Me ester (IX) of VIII, **hexagons**, m. 145° (from MeOH, Me2CO, or C6H6petr. ether) was formed by methylating IX in MeOH or VII in Me2 CO with excess CH2N2 in Et2O; under these conditions, in one instance, another cryst. compd. (X), a lactone analog of VIII, m. 185°, was formed. VI (37 g.) in 200 cc. MeOH was **stirred** and refluxed 0.5 hr. with 2N NaOH and treated dropwise with 500 cc. H2O. MeOH and 100 cc. H2O was distd. and the filtered mixt. **stirred** and treated at 35° with Me2SO4 until a spot test coloration with HO2SC6H4N2Cl was neg., then warmed to 60°, treated with 20 cc. 25% NaOH, heated 0.5 hr. at 95°, cooled, acidified with concd. HCl, and the resulting ppt. remethylated with CH2N2 in Et2O giving 39 g. IX. By prehydrogenating 0.3 g. PdCl2 in abs. MeOH, a catalyst was prepd. which was used in the 48 hr. hydrogenation at 40° of 38 g. IX suspended in 200 cc. MeOH giving 25 g. 4,4'-dihydroxy-2,2',3,3'-tetramethoxy-6,6'-carbomethoxybiphenyl (XI), rodlets, m. 135° (from C6H6-petr. ether); free acid (XIa), **hexagons**, m. 283-4° (from aq. dioxane or tetrahydrofuran-petr. ether and dried at 135°/1 mm. over **P2O5** and paraffin). 4,4'-Dihydroxybiphenyl (4.4 g.) in 30 cc. 2N NaOH was **stirred** with 3.5 cc. Me2SO4, after 0.5 hr. warmed to 80°, and any di-Me ether ppt. filtered off and washed with NaOH. The filtrate, acidified with 2N HCl, was boiled, filtered hot, and the ppt. washed with hot H2O, dried, dissolved in hot 2N NaOH, and cooled to 0° giving an insol. Na compd. which was washed (at 0°) with 2N NaOH, suspended in H2O, acidified with 2N HCl, heated, filtered, and the ppt. washed with H2O to neutrality giving 3.8 g. 4-hydroxy-4'-methoxybiphenyl, leaflets, m. 186° (from Bu2O or aq. dioxane). [4,3,5-(HO)(MeO)2C6H2]2 (XII) (hydrocoerulignone) (3.8 g.) was partially methylated in 50% dioxane under H using 2N KOH and 4 g. Me2SO4 at 10°. The mixt., acidified to pH 5-6, was poured into 900 cc. H2O, cooled to 0°, and the pptd. 4,4'-di-Me deriv. of XII filtered off. The filtrate evapd. in vacuo to incipient crystn. was cooled to 0° giving about 1.05 g. 4'-Me

deriv. of XII, m. 146° (by successive crystn. from MeOH, C6H6-petr. ether with C, and EtOH, followed by cold-finger sublimation at 135°/0.01 mm.), turning pink on exposure to air. XI (3 g.) in 21 cc. 66% dioxane at 30° methylated with 2N NaOH and Me2SO4, acidified with 2N H2SO4, extd. with Et2O, the ext. washed with aq. NaHCO3 and H2O, and dried gave a sirup, which in CHCl3 was chromatographed on alkali-free Woelm Al2O3. Elutions with CHCl3 were monitored by use of U.V. light. Three zones were noted, the fastest-moving one (di-Me hexamethoxydiphenate) was eluted completely with CHCl3. The column was cut between the remaining 2 zones, and each section was extd. with MeOH. These exts. were examd. by paper chromatography; the upper zone yielded XI. The central zone gave largely th 4-Me deriv. of XI (frequently contaminated with XI). Further sepn., described in detail, permitted the isolation of 1.7 g. 4-Me deriv. of XI, rhombs, m. 84° (after seeding the MeOH soln., and subsequent crystn. from C6H6-petr. ether and 50% MeOH), sapon. of which gave 91% 4-Me deriv. of XIa, rhombs, m. 247° (from Me2CO and aq. dioxane). The 4-Me deriv. of XI (1 g.) with 3.3 g. 2,3,4,5-Br(MeO)3C6HCO2H (cf. Mayer and Fikentscher, C.A. 50, 14643i) in 10 cc. dry MeOH was treated with 3.1 cc. 4.4N MeOK, evapd. in vacuo, heated 2 hrs. at about 100°/14 mm., powdered and dried 16 hrs. at 1 mm. over "Blaugel," mixed with 0.75 g. defatted Natur Cu C and 40 mg. Cu(OAc)2, dried at 40°/0.4 mm. over **P2O5** in a test tube placed in a drying pistol, after which the former was removed, connected with a "Blaugel" tube and heated 2 hrs. at 125-30°, cooled, repowdered rapidly, retreated with 0.1 g. Natur Cu C, and heated 2 hrs. at 170-80°. The product, taken up in the min. amt. 2N NaOH, was filtered and the filtrate heated 1 hr. on a steam bath, acidified with 18% HCl, the amorphous ppt. taken up in MeOH, esterified with CH2N2, evapd., the sirup in CHCl3 chromato-graphed on Woelm Al2O3, and eluted with CHCl3 until the fastest moving area, fluorescing brilliantly in U.V. light, was removed. The evapd. eluate, a mixt. of Me trimethylgallate, di-Me hexamethoxyphenate, and tri-Me octamethylvaloneate, was fractionated in high vacuum; (MeO)3C6H2CO2Me, b0.01 95-7°; di-Me hexamethoxyphenate, b0.01 200° (bath temp.). The distn. was interrupted after 15 min. at 240°/0.01 mm. and the resulting brown still residue purified by soln. in CHCl3 and chromatographing on Al2O3 (as above), evapg., and heating in vacuo at 200-250°, and then repeating the chromatographic procedure. The sirup resulting from the final CHCl3 eluate was sapond. with 2N KOH in MeOH, treated slowly with H2O, acidified, and the ppt. washed with H2O, and dried giving 425 mg. octamethylvaloneaic acid, 4',5,5',6,6'-hexamethoxydiphenic acid 4-(4,5,6-trimethoxy-2-carboxyphenyl) ether, m. 250°, identical crystallographically and in its soly. with the compd. prepd. previously from a natural product, and showing no m.p. depression when mixed with this compd.

CC 10 (Organic Chemistry)

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51:25257 Original Reference No. 51:4952b-i,4953a-c Amino sugar syntheses. IV. The preparation of N-acetyllactosamine (4-β-D-galactopyranosyl-2-deoxy-2-acetamino-D-glucopyranose) from lactose. Kuhn, Richard; Kirschenlohr, Werner (Max-Planck-Inst. Med. Forsch., Heidelberg, Germany). Ann., 600, 135-43 (Unavailable) 1956.

AB Lactose hydrate (I) (180 g.) at 65° yielded 159 g. oxime (II), rhombs, m. 183-5°, [α]D22 38.3° → 15.5° (after 25 hrs., c 1, H2O), 7 g. of which in 70% MeOH with ketene (0.2 mole), after evapn. and cooling, gave 2.5-3.0 g. N-Ac deriv. of II, m. 230-2° (decompn.) (from aq. MeOH), [α]D23 14.1° → 16° (after 12 hrs., c 1, H2O). The infrared spectrum shows the C:O band characteristic of N-Ac; no N-O-Ac band (at 5.55μ) was present. I (180 g.) in 300 cc. H2O and 100 cc. MeOH was converted to II, which as a sirup (without isolation) dissolved in 200 cc. pyridine was added dropwise at 100° to 180 g. anhyd. AcONa in 1.2 l. Ac2O. After 1 hr. the cooled mixt. was **stirred** into 8 l. ice H2O, the ppt. washed with cold H2O, dissolved in 750 cc. EtOH and again **stirred** with 8 l. ice H2O giving 270-300 g. crude octaacetyllactobionic acid nitrile (III), C28H37O18N.C6H6, **hexagons** (from C6H6), m. 90-3° [α]D 35.5° (c 1.3, MeOH), losing C6H6 on long drying at 75°/5 mm over **P2O5**-paraffin. III (20-22 g.) was also formed from 18 g. purified II by heating on a steam bath with AcONa and Ac2O. To 75 g. III in 350 cc. MeOH and 200 cc. M MeONa, after 10 min. at 20°, was added 110 cc. 2N AcOH followed by immediate concn. in vacuo to 110 cc. and addn. of 100 cc. H2O, passage through Amberlite IR-120, and evapn. of the eluate to a sirup from which AcOH was removed by repeated evapns. with H2O. The final sirup with 30 cc. MeOH, after 48 hrs. (especially on seeding), gave 18-20 g. 3-β-D-galactosyl-D-arabinose (IV), m. 162-9°, [α]D23 -54.5° → -62° (after 7 hrs., c 1, H2O); the mother liquors yielded another 2-3 g. IV isolated as N-phenyl(3-β-D-galactosyl-D-arabinosyl)amine (V). IV (6.2 g.) **stirred** 1.5-2 hrs. under reflux on a steam bath with 120 cc. EtOH, 2 g. PhNH2, and 50 mg. NH4Cl, and cooled gave 6.9 g. crude V, which, recrystd. from EtOH-H2O gave V.H2O, rodlets, m. 170-1°, [α]D22 34.7° (c 0.8, pyridine); the [α]D22 36° (HCONMe2), decreased imperceptibly at first to 7.5° (after 96 hrs., c 1.03); [α]D22 -16° (10 min.) → -42° (after 1 hr., c 0.93, H2O). H2O effects very rapid hydrolysis of V to PhNH2 and IV. V could be readily prepd. from sirups contg. IV (made from III). Also formed from such sirups, by the use of appropriate

amines, were the following (3-β-D-galactopyranosyl-D-arabinosyl)amines: N-p-tolyl-H2O, m. 162-4°, [α]D22 11.4° (10 min.) → 0° (5 hrs., c 1.1, pyridine); N-α-naphthyl-H2O, m. 196-8° (decompn.), [α]D23 842° (20 min., c 0.57, HCONMe2); N-β-naphthyl, 167-9° (decompn.), [α]D23 21.5° (4 min.) → 6.5° (48 hrs., solvent not given); N-benzyl (VI), m. 125-6° (sintering 107°), [α]D22 -20° (5 min.) → -29° (24 hrs., c 0.95, pyridine). V in hot H2O, heated 20 min. with BzH, after Et2O extn., gave IV in the aq. phase. V (35-40 g.) was also formed as follows (cf. Frush and Isbell, C.A. 48, 8740a): 100 g. Ca lactobionate-H2O, 5 g. (AcO)2Ba, and 2.5 g. FeSO4.7H2O was **stirred** in 750 cc. boiling H2O, cooled to 35°, **stirred** with 30 cc. 30% H2O2 (below 40°) and, after 45 min., with 30 cc. H2O2. After 3 hrs., the filtered soln. was evapd. to a thin sirup, 500 cc. MeOH added very gradually, and the pptd. Ca salts filtered off; the filtrate, treated with 9% (CO2H)2 was centrifuged, and the soln. passed through Amberlite IR-45, evapd. in vacuo, and treated with MeOH and PhNH2 giving V. In place of (CO2H)2, suitable ion-exchangers could be used. V (40 g.) in 150 cc. HCONMe2 and 8 cc. HCN warmed 1-2 hrs. at 80° was retreated with 6 cc. HCN, and after 2.5 hrs. evapd. to a sirup, treated with MeOH, reevapd., treated with 100 cc. H2O and 110 cc. 2N HCl, and hydrogenated 24 hrs. as above (taking up 3 moles H), centrifuged, extd. with Et2O to remove cyclohexanone, **stirred** with Amberlite IR-45, and the filtrate evapd. to a sirup, treated with 17.2 g. anhyd. AcONa (or 28 cc. Et3N) in 160 cc. 50%, MeOH, cooled, kept 24 hrs. at 20° with 24 cc. Ac2O, evapd., dissolved in 130 cc. H2O, passed through Amberlite IR-120, the eluate neutralized with Amberlite IR-45, filtered, decolorized with C, evapd., treated with 100 cc. MeOH, and kept 48 hrs. at 0° giving 17-18 g. N-acetyllactosamine (VII) (4-β-D-galactopyranosyl-N-acetyl-D-glucosamine), C14H25O11N.MeOH, m. 168-7°, [α]D22 50.5° → 28.5° (c 1, H2O), identical with the compd. isolated from the blood group components of Meconium (Kuhn and Kirschenlohor, C.A. 49, 4069b). VII (1.4-1.6 g.) was also prepd. analogously from 4.02 g. VI. To 6.2 g. VII in 75 cc. H2O and 250 cc. MeOH at 0° was added freshly distd. CH2N2 from 40 g. MeN(NO)CONH2 (VIII), kept 12 hrs., evapd., dissolved in 50 cc. H2O and 120 cc. MeOH, retreated with CH2N2 (from 20 g. VIII), kept 24 hrs., evapd., and treated with 10 cc. MeOH giving, after 24 hrs., 0.65 g. β-methyl-N-acetyllactosaminide (4-β-D-galactopyranosyl-2-deoxy-2-acetamino-β-methyl-D-glucopyranoside) (IX), m. 234-5° (decompn.), [α]D22 -23.1° (c 0.86, H2O); the mother liquors chromatographed showed both IX and VII by the chlorobenzidine reaction (Rydon and Smith, C.A. 46, 11290b). When CH2N2 was not distd. prior to use, these mother liquors showed the

presence of another compd., probably the α-isomer of IX.
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51:5404 Original Reference No. 51:1123a-i,1124a-c Acid-catalyzed reaction of 9-fluorenol with 9-alkylidenefluorenes. Wawzonek, S.; Dufek, E. (State Univ. of Iowa, Iowa City). Journal of the American Chemical Society, 78, 3530-3 (Unavailable) 1956. CODEN: JACSAT. ISSN: 0002-7863.
AB Fluorenone (180 g.) in 300 cc. dry C6H6 added to 1 mole PrMgBr in 300 cc. dry Et2O and 300 cc. dry C6H6, and the mixt. refluxed 3 hrs. and decompd. with NH4Cl gave 130 g. crude 9-propyl-9-fluorenol (I), m. 90-100°; the I heated 2 hrs. with 500 cc. glacial AcOH and 50 cc. concd. HCl, and dild. with an equal amt. cold H2O, the aq. layer extd. with petr. ether, and the combined org. layer and ext. worked up gave 56.1 g. 9-propylidenefluorene (Ia), b1 150-5°; the dark glassy distn. residue crystd. from EtOAc, and the resulting orange solid recrystd. successively from C6H6, EtOAc, and CCl4 yielded 2.5 g. 1-(9-fluorenyl)-1-(9-fluorenylidene)propane (II), m. 162-4° (from EtOAc); the MgSO4 used for drying the original soln. of the reaction products treated with H2O and extd. with C6H6 gave an addnl. 16.5 g. II. The crude I recrystd. twice from MeOH gave pure I, m. 125-6°; the MeOH filtrate dild. with H2O gave 11.7% 9-fluorenol (III), m. 149-51° (from C6H6). III (4.5 g.) and 5.5 g. Ia in 30 cc. glacial AcOH and 3 cc. concd. HCl refluxed 1.25 hrs., cooled, and treated with 10 cc. cold H2O, and the yellow gummy product crystd. from EtOAc yielded 2.5 g. II, m. 160-2°. Similar results were obtained using a mixt. of I and III. Crude 9-butyl-9-fluorenol (30 g.) heated with glacial AcOH and concd. HCl in the usual manner gave 21.8 g. 9-butylidenefluorene and 1 g. butane analog of II, white **hexagonal** plates, m. 158-60° (from C6H6-petr. ether and EtOAc). III (4.5 g.) and 5.5 g. 9-ethyl-9-fluorenol refluxed with glacial AcOH and concd. HCl gave 8.0 g. ethane analog (IV) of II, m. 139-41° (from EtOAc, CCl4, and EtOAc). III (4.5 g.) and 5.5 g. 9-methyl-9-fluorenol gave similarly 4.0 g. 9-fluorenyl-9-fluorenylidenemethane (V), m. 206-8° (from C6H6-petr. ether and EtOAc). II (1 g.) in 50 cc. glacial AcOH refluxed 1.75 hrs. with 47% HI (d. 1.50) yielded 0.63 g. ethyldi(9-fluorenyl)methane, long white needles, m. 158-60° (from C6H6-petr. ether). V (0.20 g.) gave similarly 0.15 g. di(9-fluorenyl)methane (VI), long white needles, m. 212-13° (from C6H6-petr. ether). 9-Chloromethylfluorene (VII) (0.8 g.) in ligroine (b. 60-8°) added to 9-fluorenyllithium from 1 g. Li and fluorene (VIII), the mixt. refluxed 12 hrs., decompd. with abs. EtOH, and steam distd., and the distn. residue triturated with hot EtOH gave 0.6 g. VI, m. 212-13° (from C6H6-petr. ether). 9-Fluorenylcarbinol (15 g.) refluxed 0.5 hr. with 45 cc. SOCl2 and distd. gave 5.6 g. VII, m.

66.5-7.5° (from EtOH), b1-3 140-5°; the crude product from another run dissolved in Et2O and washed with H2O yielded 100% bis(9-fluorenylmethyl) sulfite, m. 106-7°. II (1.0 g.) in EtOAc treated at -40° with ozone, the soln. treated with H (40 lb.) in the presence of PtO2, and the solvent removed yielded 0.05 g. of Et 9-fluorenyl ketone, m. 93-6° (from EtOH); a similar ozonide soln. decompd. with Pd catalyst gave only III, m. 149-51°, and fluorenone (VIIIa) (2,4-dinitrophenylhydrazone, m. 300° decompn.). II (0.20 g.) in 20 cc. glacial AcOH refluxed 1 hr. with 1.2 g. K2Cr2O7 and 1 cc. concd. H2SO4, cooled, and dild. with 50 cc. H2O gave 0.15 g. VIIIa, m. 80-3°. II (0.5 g.) in 10 cc. C6H6 and 15 cc. 98-100% HCO2H kept 36-48 hrs. at room temp. with 2 cc. 30% H2O2 yielded 0.35 g. Et 9-(9,9'-bifluorenyl) ketone (IX), m. 211-12° (from aq. EtOH). IV oxidized in the same manner gave the Me ketone analog of IX, m. 160-1° (from EtOH). IX (0.3 g.) refluxed 3 hrs. with KOEt from 3.3 g. K in 20 cc. EtOH and cooled deposited 0.2 g. 9,9-bifluorenyl, long white needles, m. 244-5° (from C6H6 and petr. ether). Liquid NH3 (15 cc.) added to 1.9 g. 9-chlorofluorene and 2.2 g. Et 9-fluorenyl ketone (X) in 10 cc. dry PhMe, allowed to stand overnight, and evapd. in vacuo yielded 0.8 g. IX, m. 212-13° (from 95% EtOH). KOMe from 10.5 g. K, 43 g. VIII, and 27.6 g. EtCO2Et in 80 cc. Et2O refluxed 20 hrs., poured into 225 cc. H2O, acidified with 3N HCl, and extd. with Et2O yielded 24.6 X, long white needles, m. 101°; 2,4-dinitrophenylhydrazone, m. 170-70.5° (from EtOH). IX (0.5 g.) in 10 cc. abs. Et2O added to 0.2 g. LiAlH4 in 20 cc. abs. Et2O, decompd. with EtOAc and dil. HCl, and worked up in the usual manner gave 0.3 g. ethyl-9-(9,9'-bifluorenyl)carbinol, m. 181-2° (from C6H6-petr. ether). VIII (27.7 g.) in 85 cc. xylene added to 0.42 mole EtMgBr in 300 cc. Et2O, refluxed 3 hrs. while distg. off slowly the Et2O, the residual xylene soln. treated with 50 cc. Et2O and 50 cc. xylene, the resulting solid refluxed 2.5 hrs. with 4.8 g. EtCO2Et in 50 cc. Et2O, and the mixt. decompd. with NH4Cl and extd. with Et2O yielded 3.2 g. VIII; the remaining oil distd. yielded 0.8 g. mixt. of Ia and X, b1 132-8°, and 0.5 g. X, b1 138-45°, m. 101°; the dark red distn. residue crystd. from EtOAc yielded 1.0 g. II, m. 161-4°. 9-Carbethoxy-9,9'-bifluorenyl (2.2 g.) in 30 cc. dry Et2O **stirred** 1 hr. with 1.2 g. LiAlH4, treated with excess EtOAc, and acidified with dil. HCl, and the Et2O layer worked up gave 1.1 g. 9-(9,9'-bifluorenyl)carbinol (XI), white crystals, m. 174-5°. XI (1.0 g.) in 20 cc. dry xylene refluxed 4 hrs. with 5.0 g. **P2O5**, the soln. cooled and decanted, the residue extd. with a small amt. of hot C6H6, the combined C6H6 and xylene solns. washed, filtered, and evapd. to dryness in vacuo, and the residue recrystd. twice from C6H6-petr. ether gave 0.64 g. 9-(9'-fluorenyl)phenanthrene, m. 196-8°. I (2.5 g.) in 40

cc. warm glacial AcOH treated with 80 cc. SnCl2-iodine soln. (prepd. by adding 10 g. SnCl2 in 20 cc. concd. HCl to 5 g. iodine in 80 cc. warm glacial AcOH), the mixt. **stirred** 1.5 hrs., and the orange ppt. crystd. from Et2O gave 0.9 g. 9,9'-dipropyl-9,9'-bifluorenyl, white crystals, m. 208-9°. 9-Butyl-9-fluorenol (2.5 g.) gave similarly with SnCl2 and iodine 0.8 g. 9,9'-dibutyl-9,9'-bifluorenyl, m. 202° (from EtOAc).

CC 10 (Organic Chemistry)

L57 ANSWER 11 OF 20 HCA

51:1788 Original Reference No. 51:387c-i,388a-i,389a Condensation products of phenols and ketones. X. The structure of Dianin's compound, a unique inclusion-forming substance. Baker, Wilson; Floyd, A. J.; McOmie, J. F. W.; Pope, G.; Weaving, A. S.; Wild, J. H. (Bristol Univ., UK). Journal of the Chemical Society, Abstracts 2010-17 (Unavailable) 1956. CODEN: JCSAAZ. ISSN: 0590-9791.

AB cf. C.A. 47, 8678b. A product, "Dianin's compd.," 1st prepd. in 1914 (cf. C.A. 9, 1903), from PhOH and Me2C:CHCOMe, is shown to be 4-p-hydroxyphenyl-2,2,4-trimethylchroman (I). Oxidation yields 2,2,4-trimethylchroman-4-carboxylic acid (II), and thermal degradation gives PhOH and 2,2,4-trimethylchromene (III). The latter compd. has been synthesized and yields I by addn. of PhOH. I forms inclusion compds. with over 50 widely different org. solvents, some inorganic gases and with iodine. The large, separate cavities in the crystals are defined by six mols. of I and the ratio of no. of mols. of I to the no. of included mols. is generally 6:1, though a ratio of 3:1, i.e., 2 mols. per hole, is found for a no. of small mols. PhOH (400 g.) and 100 g. Me2C:CHCOMe was satd. 8 hrs. with a stream of anhyd. HCl, the resulting red viscous mixt. kept dry 4 days at 38°, then 1 l. boiling H2O added, the mixt. well shaken and heated on a water-bath, the top aq. layer decanted and lower layer similarly treated with 1 addnl. l. hot H2O and decanted, the resulting oily product shaken with 250 ml. hot EtOH, cooled, the resulting cryst. EtOH adduct collected, and twice **stirred** with 150 ml. portions cold EtOH yielding 115-30 g. (40-5%) **hexagonal** crystals, m. 165-6° after crystn. from EtOH. The EtOH complex (30 g.) was dissolved in 200 ml. hot 2N NaOH, boiled 15 min., CO2 passed through for 30 mins., the ppt. boiled twice with 200 ml. portions H2O, and dried in vacuo over **P2O5** yielding 26 g. I, fine needles, m. 156-7° The EtOH complex was also slowly sublimed at 140°/0.1 mm. yielding unsolvated I, large irregular prisms, m. 155-6°. I is sol. in hot aq. KOH and on cooling gave a crystn. alkali salt. A satd. boiling soln. of KMnO4 in 1200 ml. Me2CO was added rapidly to a soln. of 3 g. EtOH adduct of I in 100 ml. Me2CO contg. a few crystals of FeSO4, the Me2CO removed by distn., the residue shaken with 100 ml. H2O, 20 g. Na2S2O5, and 20 ml. 2N HCl, and SO2 passed through until all the MnO2 had dissolved, the mixt. then extd. with

3 + 50 ml. Et2O, the Et2O exts. shaken 3 times with satd. aq. Na2CO3, the alk. soln. acidified, the resulting ppt. boiled with 4 + 30 ml. petr. ether, the petr. ether ext. concd. to 5 ml., and cooled to 0° yielded a sticky solid; 2 crystns. from the same solvent gave 0.16 g. II, irregular prisms, m. 124-5°. II, on treatment with cold concd. H2SO4, dissolved slowly with evolution of CO, at 40°, the reaction was brisk. The nonacidic material in the oxidation with 2,4-dinitrophenylhydrazine in alc. H3PO4 gave the 2,4-dinitrophenylhydrazone of 2,2-dimethylchromanone, orange-red needles, m. 222-3°. Methylation of the EtOH adduct of I, suspended in Me2CO, with excess Me2SO4 and KOH gave 87% ether, b0.5 140-1°, which solidified after 4 weeks as rectangular tablets, m. 50-1° (from petr. ether). The tribromo deriv., needles, prepd. at room temp. with excess Br and AcOH during 18 hrs., m. 103-4°(from EtOH). The EtOH adduct of I (40 g.) was refluxed 2 hrs. at 300° yielding an oil which was twice distd., shaken with 100 ml. 10% NaOH, and extd. with 3 + 50 ml. Et2O yielding 18.5 g. III, b17, 114-15°, nD20 1.5502. III (0.5 g.) was treated dropwise at room temp. with 3 ml. Br, left overnight, the semi-solid product dissolved in CHCl3, the soln. shaken with aq. NaHSO3, dried, the residue crystd. twice from petr. ether yielding 1.18 g. 3,3,4,6,8-pentabromo-2,2,4-trimethylchroman, rectangular prisms, m. 145-6°. Excess satd. aq. KMnO4 was dropped into a **stirred** suspension of 2 g. III in 20 ml. 1% aq. KOH, the soln. acidified, decolorized with SO2, then satd. with NaCl, and extd. with Et2O, and resulting oil gave a 2,4-dinitrophenylhydrazone of o-(2-formyl-1-methylethoxy)actophenone, orange-red plates, m. 203-4° (from MeOH). Similar results were obtained by the oxidation of 1 g. III with 3 g. Cr2O3 in 10 ml. H2O and 20 ml. AcOH.

III (1 g.) was also ozonized 1 hr. at -20° in 20 ml. dry CCl4, the solvent removed in vacuo, and the oil isolated as usual giving the o-hydroxyacetophenone; 2,4-dinitrophenylhydrazone, m. 212-13° (from EtOH). β,β-Dimethylacryloyl chloride (7.5 g.) was added dropwise to 6 g. PhOH, the mixt. heated 4 hrs. on a steam-bath, cooled, 100 ml. H2O added, and the oily product extd. with Et2O giving 8.8 g. phenyl β,β-dimethylacrylate, b11 127°. This ester (2 g.) was slowly added to 2.1 g. powd. AlCl3, the mixt. heated 2 hrs. at 90° cooled, 25 ml. 2N HCl added, the mixt. extd. with Et2O, and the Et2O ext. washed with 1% NaOH and H2O yielding 0.9 g. 2,2-dimethylchromanone (IV), prisms, m. 87-8° (from petr. ether); 2,4-dinitrophenylhydrazone, m. 220-1° (from EtOH). 4-Methylcoumarin (10 g.) in 200 ml. Et2O was added during 1 hr. to MeMgI prepd. from 12.2 g. Mg and 71 g. MeI in 100 ml. Et2O, the mixt. boiled 10 hrs., then poured into 200 ml. 20% HCl contg. 200 g. ice, extd. with Et2O and the partial solid crystd. from petr. ether yielding 1.2 g. 4-o-hydroxyphenyl-2-methylpent-3-en-2-ol (V), needles, m. 97-8°. V, on distn.

gave 73% III, b28 124-6°, nD20 1.5511, and the same pentabromide, m. 145-6°. V (0.8 g.) was cyclized by boiling 0.5 hr. with 10 ml. AcOH and 0.25 ml. concd. H2SO4, the soln. dild. with H2O, the product collected in Et2O and dist. yielding 0.48 g. IV. Dry HCl was bubbled 1 hr. through a cooled mixt. of 1.65 g. PhOH and 1.5 g. IV, and after 5 days the cryst. mass worked up as before giving 1.23 g. EtOH adduct of I, m. 163-4°; benzoate, m. 160-1° (from EtOH). A mixt. of 2.25 g. o-cresol and 2.5 g. III was satd. with HCl for 1 hr., after 12 days the partly cryst. mass extd. with 5 + 20 ml. boiling H2O, the residue steam dist., and the residue collected in Et2O yielding 2.4 g. 4-(4-hydroxy-3-methylphenyl)-2,2,4-trimethylchroman, needles, m. 135-6°; acetate, irregular prisms, m. 121-2°. Cryst. adducts of I were prepd. by crystn. of unsolvated I from the various liquid solvents. With MeI, I was placed in the thimble of a Soxhlet app. and extd. with MeI, the adduct sepd. as the solvent became satd. The iodine adducts were prepd. by using decalin as solvent. With NH3 and SO2, I was dissolved in the liquified gases, and the solns. decanted from the undissolved solids and allowed to evaporate. The adducts were analyzed by drying the complexes 4 hrs. at 100°/0.1 mm., then weighed samples heated 5-10 min. at 190-200° and again weighing. Samples of the adducts with aliphatic acids were dissolved in EtOH and titrated with 0.02N NaOH. The iodine adduct in EtOH was titrated with 0.01N Na2S2O3. Cryst. adducts of I, with solvent used, m.p., and moles I/mole solvent were: MeOH, 155-6°, 2; EtOH, 163-4°, 3; iso-PrOH, 160-1° 3; BuOH, 159-60°, 3; tert-BuOH, 166-7°, 3; Me2CO, 159-60°, 3; CCl4, 159-60°, 3; CH2Cl2, 167-8°, 3; MeI, 166-7° 3; MeNO2, 164-5°, 3; HCO2H, 159-60°, 3; AcOH, 161-2°, 3; EtCO2H, 156-7°, 4; CHCl3, 161-2°, 4; CS2, 164-5° 4; C3H7CO2 H, 162-3° 5; AmOH, 169-70°, 6; C6H13OH, 162-3°,6; Et2O, 172-3°6; BrCH2CH2CH2Br, 168-9° 6; C2H4Cl2, 163-4°, 6; C2H4Br2, 165-6°, 6; CCl2:CCl2, 153-4°, 6; BuBr, 169-70°, 6; biacetyl, 162-3°, 6; C4H9CO2H, 169-70°, 6; C5H11CO2H, 160-70°, 6; Et2NH, 164-5°, 6; CH2ClCO2Et, 171-2°, 6; C6H6, 160-1°, 6; PhMe, 155-6°, 6; o-MeC6H4OH, 154-5°, 6; m-MeC6H6OH, 153-5° 6; p-MeC6H4OH, 152-3°, 6; PhBr, 158-9°, 6; PhI, 152-4°, 6; o-ClC6H4Cl, 150-1°, 6; diisobutylene, 157-8°, 7; tert-AmOH, 161-2°, 7; AcOEt, 167-8°, 7; C4H9CO2Am-iso, 160-1°, 7; p-BrC6H4OMe, 154-5° 7; m-ClC6H4Cl, 158-9°, 7; 2-bromopyridine, 154-5°, 7; 2,6-lutidine, 164-5°, 7; 3-methylheptane, 174-5°, 8; 1-MeC10H7, 157-8° 8; pyridine, 159-60°, 8; Et3N, 158-59°, 9; Decalin, 157-8°, 9; Decalin, 150-7° 17; SO2, 152-3°, 4; NH3, 161-2°, 6; and iodine, 154-5°, 7.

CC 10 (Organic Chemistry)

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50:64440 Original Reference No. 50:11997f-i,11998a-i,11999a-g
Substituting addition of maleic anhydride to partially hydrogenated naphthalenes and to fluorene. Alder, Kurt; Wollweber, Hartmund; Spanke, Wilhelm (Univ. Cologne, Germany). Ann., 595, 38-54 (Unavailable) 1955. OTHER SOURCES: CASREACT 50:64440.
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 47, 3826f. 1,4-Dihydronaphthalene (I), b11 86-7°, free from isomers, was prepd. in nearly quant. yield by Hansky's method (U.S. 2,473,997, C.A. 43, 7510g). The addn. of maleic anhydride (II) to I under widely varying conditions showed that, to obtain a stereochemically homogeneous product, a temp. of 120-30° could not be exceeded. I (22 g.) in 20 cc. C6H6 heated 9 days at 110-20° with 22 g. II gave over 12 g. (1,2-dihydro-2-naphthyl)succinic anhydride (III), m. 161-2° (from AcOH), unstable toward alk. KMnO4. The structure of III was detd. unequivocally. I (30 g.) and 40 g. II in 50 cc. C6H6 heated 20 hrs. at 190-200° gave about 48 g. of a mixt. (IV) of III and an isomer, m. 140-60°, and 10-12 g. of a resinous still residue. Repeated crystn. of IV from AcOEt gave pure III. On adding III in Me2CO to a boiling soln. of Na2CO3 at such a rate that the Me2CO distd. regularly during the addn., then cooling, extg. with Et2O, and acidifying the aq. soln., the free acid, C14H14O4 (IIIa), sepg. as an oil that crystd. slowly (no m.p. given). III (5 g.) in 200 cc. AcOEt, hydrogenated with PtO2 as catalyst, gave (1,2,3,4-tetrahydro-2-naphthyl)succinic anhydride (V) (termed "ac-β-tetralylsuccinic anhydride"), m. 163° (giving a m.p. depression when mixed with III); free acid, corresponding to V, m. 159-60° (from AcOEt) (di-Me ester, m. 72°). Dehydrogenation of III with S at 180-230° gave small amts. of C10H8 and (2-naphthyl)succinic acid, m. 229°. III (7 g.) esterified with CH2N2 in MeOH, the soln. evapd., the residue ozonized in AcOEt at -20° to -30°, poured into a small amt. of H2O contg. H2O2, exposed to air several days, dissolved in aq. Na2CO3, the soln. extd. with Et2O, and the aq. layer acidified and reextd. with Et2O gave 5 g. of an oil, which was decarboxylated by refluxing 2 hrs. with 10 cc. quinoline and 0.8 g. Cu chromite catalyst, adding a 2nd portion of catalyst, cooling, and extg. with Et2O. This ext., washed with 18% HCl and H2O, and evapd., gave an oil that was oxidized further by soln. in NaOH and treatment with satd. KMnO4 soln. until the color persisted, boiled with MeOH, filtered, and the filtrate concd. and acidified, giving BzOH. Thus III could not have been a 1,4-dihydronaphthalene deriv., otherwise the final product would have been o-C6H4(CO)2O. A mixt. of 25 g. 2-tetralone (Cornforth, et al., C.A. 37, 878.9), 25 g. di-Me bromosuccinate, 75 cc. C6H6, 10 g. Zn-Hg, and a trace of iodine

stirred and heated on the steam bath, cooled, treated with 200 cc. ice-cold H2SO4, extd. with Et2O, the ext. dried, evapd., freed from tetralone and Me fumarate by distg. at 150°/13 mm., the still residue refluxed 1 hr. in 50 cc. C6H6 with 5 g. **P2O5**, treated with 50 cc. H2O, extd. with Et2O, the ext. evapd., and the residue sapond. with KOH in MeOH and acidified, gave (3,4-dihydro-2-naphthyl)succinic acid (VI), m. 250° (from AcOH), giving a marked m.p. depression when mixed with either IIIa or (2-naphthyl)succinic acid. VI was unsatd. toward alk. KMnO4. Its synthesis confirms the structures assigned to III and IIIa. III (10 g.) in 150 cc. PhNO2 cooled, treated gradually with 9 g. AlCl3 in 50 cc. PhNO2, **stirred** 3 hrs. at room temp., the mixt. decompd. with ice-HCl, extd. with Et2O, the ext. shaken with satd. aq. NaHCO3, and the aq. soln. acidified gave almost quantitatively the oxo acid (VIIa), m. 198° (from dil. AcOH). When the mixt. IV was cyclized similarly, the (VIIa) (XII) main product was VIIa, together with smaller amts. of the diastereomer (VIIb), m. 204-5° (from aq. AcOH), of VIIa. A mixt. of VIIa and VIIb gave a sharp m.p. depression. The Me ester of VIIa m. 139°. VIIa (4 g.) reduced by Martin's modification of the Clemmensen reaction (C.A. 30, 6726.1) gave a mixt. which on fractional crystn. from MeCN yielded the less sol. 3-carboxy-4,9-dihydro-5,6-benzindan (VIII), m. 168° (unstable toward KMnO4), and, from the mother liquors, the 7,8-dihydro deriv. (IX) of VIII, m. 138° (unreactive toward KMnO4). The original mixt. (4 g.) of VII and IX heated with Pd-C at 280-350° until the loss of CO2 and H was complete (2 hrs.), the cooled, powd., dark still residue extd. with AcOEt, the ext. evapd., and the residual oil made faintly alk. and steam distd. gave 5,6-benzindan (X), m. 94° (picrate, orange needles, m. 119°). VIIb reduced like VIIa, and the resulting mixt. similarly decarboxylated and dehydrogenated also gave X. I (11.3 g.) and 11 g. (.tplbond.CCO2Me)2 in 15 cc. C6H6 heated 40 hrs. at 120-30° in a sealed tube, and the product distd. in vacuo gave a brittle still residue and 16.5 g. of an oil b12 225°, which, sapond, with KOH in MeOH, yielded 60% (2-naphthyl)succinic acid, forming, when boiled with AcCl, the anhydride (XI), m. 134° (from C6H6). XI (3 g.) cyclized at room temp. with 4 g. AlCl3 in PhNO2, as in the case of III, gave an oxo acid (XII), reduced by the modified Clemmensen method (with xylene in place of PhMe) to 1-carboxy-4,5-benzindan, m. 148° (from dil. AcOH) which was decarboxylated with Cu chromite at 260-70°, to 4,5-benzindan (XIII), colorless liquid (orange-yellow picrate, m. 110°). The anhydride of VI, cyclized with AlCl3 and PhNO2 and the product reduced with Zn-Hg and HCl and then dehydrogenated and decarboxylated with Pd-Cu gave XIII. Similarly 10 g. (2-cyclohexen-1-yl)succinic anhydride (C.A. 44, 2925f) was cyclized to an oily oxo carboxylic acid, reduced with Zn-Hg and HCl to an oil which was esterified with CH2N2, then heated 3 hrs. with Pd-C at

310-20°, the product extd. with Et2O, the ext. evapd., and the residue sapond., and acidified, giving 1-carboxyindan, identified as the anilide (XIV), m. 140° (cf. Hardy, C.A. 30, 4120.1). Phenylsuccinic anhydride was cyclized with AlCl3 in PhNO2 to 1-carboxy-3-indanone-H2O, m. 84° (120° (after drying in vacuo)) (cf. Speight, et al., C.A. 19, 494), reduced to 1-carboxyindan, forming XIV. Fluorene (XV) (34 g.) and 20 g. II heated 8 hrs. at 220°, freed from residual II by heating in vacuo, the comminuted residue treated with an excess of hot aq. Na2CO3, cooled, filtered, and the filtrate extd. with Et2O to remove XV and acidified gave 27 g. (9-fluorenyl)succinic acid (XVI), needles or small blocks, m. 188° (from MeCN, then AcOEt); di-Me ester, needles, m. 119°. XVI (40 g.) was converted into the anhydride, m. 167° (from AcOEt), by refluxing 3 hrs. with 240 cc. AcCl. The original mixt., without isolating the anhydride, treated with 150 cc. PhNO2, freed from AcCl by distn. in vacuo, **stirred** 4 hrs. at room temp. with 44 g. AlCl3 in 150 cc. PhNO2, poured into a mixt. of 400 g. ice, 400 cc. HCl, and 200 cc. Et2O, shaken vigorously, and allowed to stand a long time gave 13 g. of the cis-XVII (XVIIa), brittle **hexagons**, m. 239° (from MeCN, then AcOEt). The Et2O soln. washed with dil. HCl and H2O and extd. with aq. NaHCO3 gave a ppt. of mixed Na salts which redissolved in more H2O; this soln. treated with C, filtered, and acidified yielded 17 g. of a mixt. of XVIIa and the trans-XVII (XVIIb), which, extd. repeatedly with Et2O, gave pure XVIIb, waxy rhombs or prismatic needles, m. 207° (from MeCN, then AcOEt). The Et2O-insol. residues gave more XVIIa. The yield ratio of XVIIb to XVIIa was 1:2; when the AlCl3-PhNO2 treatment was carried out on the steam bath in lieu of at room temp., this ratio was 1:1. The Me ester of XVIIa, leaflets, m. 125° (from AcOEt ligroine), was formed with MeOH and H2SO4. The Me ester of XVIIb m. 134°. XVIIb (5 g.) underwent a Clemmensen (24 hrs.) reduction with 10 g. amalgamated Zn foil, 30 cc. HCl, 15 cc. H2O, 5 cc. AcOH, and 40 cc. xylene, followed by 2 further addns. of 30 cc. HCl each; the mixt. extd. with C6H6-Et2O (1:1), the washed ext. treated with satd. NaHCO3 soln. and the NaHCO3 soln. acidified gave 4 g. trans-1,2,3,4-tetrahydro-2-carboxyfluoranthene (XVIIIb), needles, m. 166° (from C6H6-ligroine, 1:2); Me ester, m. 98°. Treated similarly with very slight, fully described modifications, XVIIa gave 75% of the cis-isomer (XVIIIa) of XVIIIb, m. 231° (from AcOEt-ligroine); its Me ester, m. 99-100°, refluxed with MeONa in MeOH and acidified gave XVIIIb, m. 166° (whose ester was not isomerized when treated similarly). The Me ester of XVIIIb (1.8 g.) heated 3 hrs. under N at 260-90° with 0.7 g. Pd-C, gave the calcd. amt. of H and about 67% of the calcd. amt. of CO2; the cooled residue extd. repeatedly with AcOEt, the ext. evapd., sapond. with 10% KOH in MeOH, and the mixt. treated with H2O, concd., and extd. with Et2O

yielded 0.5 g. fluoranthene (XIX), m. 110°. The aq. phase when acidified gave 0.7 g. 2-carboxyfluoranthene, yellow needles, m. 219° (from AcOEt-ligroine). Treated similarly, 2.5 g. XVIIIa at 240-320° gave about 84% XIX, but only traces of its 2-carboxy deriv. 18 references.

CC 10 (Organic Chemistry)

L57 ANSWER 13 OF 20 HCA COPYRIGHT 2004 ACS on STN

50:44494 Original Reference No. 50:8580c-i,8581a-i,8582a-e Polynuclear aromatic hydrocarbons. IV. Benzo[c]phenanthrenes. Phillips, Donald D.; Johnson, A. Wm. (Cornell Univ., Ithaca, NY). Journal of the American Chemical Society, 77, 5977-82 (Unavailable) 1955. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 50:44494.

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 50, 4887c. A new method for the prepn. of benzo[c]phenanthrene derivs. has been developed; advantage was taken of the polyfunctional nature of the readily available β-methallylsuccinic anhydride (I) which, when treated with C6H6 in the Friedel-Crafts reaction (II), gives rise to the oxo acids Me2PhCCH2CH(CO2H)CH2Bz (III) and 4,4-dimethyl-1-tetralone-2-acetic acid (IV), both of which may be converted in good over-all yield to the gem-di-Me deriv. 5,5-dimethyl-5,6-dihydrobenzo[c]phenanthrene (V), and thence to 5-methylbenzo[c]phenanthrene (VI). Compds. analogous to V are of interest as potential carcinogenic agents and may prove useful in establishing the role of coplanarity in carcinogenesis among polynuclear aromatic hydrocarbons. Me2C:CH2 (134 g.), 100 g. maleic anhydride, and 100 cc. C6H6 heated at 180° in a steel bomb, the mixt. kept 4 hrs. at 180°, the excess olefin and C6H6 removed at atm. pressure, and the residue distd. in vacuo gave 98.5 g. I, b9 137-8°, m. 61-2°; and 8-10 g. γ-methyl-γ-valerolactone-2-acetic acid (VII), b2 140-80°, m. 141-2°. I (60 g.) in 200 cc. C6H6 added with stirring to 171 g. AlCl3 in 200 cc. C6H6 during 0.5 hr. at 0-5°, the mixt. **stirred** 48 hrs. at room temp. under a stream of N, the mixt. worked up, and the resulting acidic material (47 g.) esterified with MeOH and HCl and distd. gave 5.0 g. unidentified material, b1.3 98-104°, nD20 1.4980, d21 1.089 [2,4-dinitrophenylhydrazone, red crystals, m. 149.5-50.5° (from EtOH-EtOAc); it gave sapond. an acid, m. 92-4°]; 16.0 g. Me ester (VIII) of IV, colorless needles, m. 60-1.5° (from aq. EtOH) [2,4-dinitrophenylhydrazone, yellow-orange crystals, m. 159-61° (from EtOH)]; and 7.2 g. Me ester (IX) of III, b0.3 175-8°, nD20 1.5475. VIII treated with N2H4 gave the characteristic dihydropyridazone (X), colorless plates, m. 172.5-3.5° (from EtOH). VIII sapond. gave IV, fine colorless needles, m. 120-1° (from Me2CO-hexane). IX treated with N2H4 gave the corresponding dihydropyridazone, colorless needles; and yielded sapond. II, colorless microcryst.

powder, m. 106.5-8.0° (from Me2CO-hexane). I (20 g.) in 75 cc. C6H6 added with stirring to 67 g. SbCl5 and 250 cc. C6H6 at 0° during 2 hrs., the mixt. **stirred** 18 hrs. at room temp., decompd., washed with acid, extd. with aq. carbonate to give 1.5 g. VII, the C6H6 layer evapd., and the brown semisolid residue (13.3 g.) crystd. from aq. EtOH gave α-phenacyl-γ-methyl-γ-valerolactone (XI), colorless plates, m. 69-70°; 2,4-dinitrophenylhydrazone, orange microneedles, m. 226-7° (from EtOAc). XI (4.0 g.) in 75 cc. C6H6 treated at 0° with 5.8 g. AlCl3, and the complex **stirred** at room temp. overnight and worked up in the usual manner gave 0.52 g. unchanged XI and 4.5 g. III, m. 95-100°. III (5.0 g.) in 70 cc. abs. EtOH contg. 1.0 g. 10% Pd. hydrogenated 4 hrs. at 60° and 45 lb. pressure, the mixt. filtered and evapd., and the residue (4.66 g.) treated with p-BrC6H4COCH2Br gave the p-bromophenacyl ester of Me2PhCCH(CO2H)2(CH2)2Ph (XII), fine colorless needles, m. 93.5-4.5°. XI (2.0 g.) in 75 cc. abs. EtOH hydrogenated in the same manner, and the resulting oily lactone condensed with C6H6 and 2.0 g. AlCl3 gave 1.4 g. XII. CH2:CMeCH(CO2H) (XIII) condensed with ethylene oxide yielded 50% α-(β-methallyl)-γ-butyrolactone (XIV), b2.25 85-7°. XIV treated with ClCH2CH2OH yielded α-(2-hydroxyethyl)-γ-methyl-γ-valerolactone, b0.6 118-20°, nD23 1.4578. XIV (17.5 g.) in 75 cc. C6H6 treated with cooling and stirring with 44.5 g. AlCl3, the mixt. kept 12 hrs. at room temp. and decompd. in ice and acid, the Et2O layer extd. with aq. Na2CO3, the aq. alk. ext. acidified to give 0.5 g. XII, the Et2O soln. evapd., and the residual neutral material (13 g.) crystd. from hexane gave α-(2-methyl-2-phenylpropyl)-γ-butyrolactone (XV), **hexagonal** plates, m. 57-8°. XV treated at 80° with excess C6H6 and AlCl3 gave almost 100% XII. XII (8.9 g.) added to 6.96 g. PCl5, the POCl3 codistd. with three 15-cc. portions C6H6, the crude residue dissolved in 30 cc. dry C6H6, the soln. added at 0° during 20 min. to 5.7 g. AlCl3, the mixt. **stirred** 5 hrs. at 20° and decompd. in the usual manner yielded 7.4 g. oily mixt. (XVI) of 2-(2-methyl-2-phenylpropyl)-1-tetralone and 2-(2-phenylethyl)-4,4-dimethyl-1-tetralone; 2,4-dinitrophenylhydrazone, orange feltlike needles, m. 233-4° (from EtOH-EtOAc). XVI (7.0 g.) in 25 cc. dry Et2O added at room temp. to 0.48 g. LiAlH4 in 35 cc. Et2O, the mixt. refluxed 2 hrs., and decompd. with H2O and acid, the Et2O layer evapd., and the residual oil (7.0 g.) crystd. from aq. EtOH gave a mixt. (XVII) of 2-(2-methyl-2-phenylpropyl)- and 2-(2-phenethyl)-4,4-dimethyl-1-tetralol, colorless, needles, m. 94.5°, 99-100°. XVII (1.36 g.) and 0.36 g. **P2O5** heated 25 min. at 110° and 10 mm., the mixt. dild. with H2O and extd. with Et2O, and the ext. chromatographed on Al2O3 gave 0.76 g. mixt. (XVIII) of 3-(2-methyl-2-phenylpropyl) and 3-(2-phenethyl)-1,1-dimethyl-1,2-

dihydronaphthalene, colorless oil, nD18 1.5820. XVII (1.5 g.) treated dropwise at room temp. with 2.0 cc. concd. H2SO4, the dark soln. swirled 3 min., poured quickly onto ice and H2O, and extd. with Et2O, the ext. washed, dried, and evapd., and the crude residue chromatographed on Al2O3 gave 1.2 g. oily 4:1 mixt. of 5,5-dimethyl-5,6,6a,7,8-13-hexahydrobenzo[c] phenanthrene (XIX) and XVIII. An intimate mixt. of 0.51 g. XIX and XVIII heated 4 hrs. at 300° with 70 mg. 10% Pd-C, and the melt chromatographed on Al2O3 in hexane yielded 0.33 g. V, colorless fluorescent oil; it developed a color with 2,4,7-trinitrofluorenone (XX). V (0.56 g.) and 0.11 g. 30% Pd-C heated 2 hrs. at 360°, and the melt dissolved in hexane and chromatographed on Al2O3 gave 0.30 g. unchanged V and 0.21 g. VI, colorless, fluorescent oil; picrate, orange needles, m. 125-6° (from 95% EtOH); VI-XX complex, reddish orange needles, m. 151-3° (from AcOH). I (10 g.) in 50 cc. 6N HCl heated to soln. during 10 min. and then cooled deposited 7.8 g. VII, colorless crystals, m. 137-40° (recrystd. from C6H6, m. 141-3°). VII (15 g.) in 17 cc. C6H6 treated with stirring during 0.5 hr. with 29 g. AlCl3, and the mixt. warmed to about 50°, **stirred** 7 hrs. at room temp., and worked up in the usual manner gave 19.7 g. Me2PhCCH2CH(CO2H)CH2CO2H (XXI), microcryst. powder, m. 142-4°. XXI (10 g.) and 10.2 g. Ac2O refluxed 1 hr., the excess Ac2O and AcOH distd. in vacuo, the crude anhydride dissolved in C6H6, the soln. treated at 0° with 11.2 g. AlCl3 during 0.5 hr., and the complex decompd. in the usual manner yielded 7.9 g. IV, m. 113-16° (recrystd. from Me2CO-hexane), m. 120-2°. NaOEt (from 0.15 mole Na) and 8.9 g. HCO2Et in 150 cc. cold dry Et2O treated with stirring at 0° with 17.4 g. 4,4-dimethyl-1-tetralone, the red soln. **stirred** 3 hrs. at room temp. and dild. with H2O and ice, the Et2O evapd. to give 6.3 g. unchanged tetralone, and the aq. layer worked up gave 8.2 g. formyl deriv. (XXII), b4 139.5-40°, nD25 1.6020. XXII (5.0 g.) treated in the cold with stirring with 2.4 g. dry NaOEt in 100 cc. dry C6H6, the mixt. **stirred** 1 hr. at 25°, treated with 7.0 g. BrCH2CO2Et in 15 cc. C6H6, **stirred** 2 hrs. at 25°, refluxed 20 hrs., and dild. with H2O, the excess solvent removed, the residual crude oil refluxed 4 hrs. with 100 cc. 10% aq. NaOH, and the mixt. acidified gave 2.7 g. alkylated formyl deriv. and 1.4 g. IV, colorless microneedles, m. 120-1°. VIII (10.0 g.) in 100 cc. dry Et2O treated during 1 hr. with 0.04 mole PhMgBr in 50 cc. Et2O, and the soln. refluxed 45 min. and decompd. in the usual manner yielded 8.8 g. lactone XXIII, m. 147-50° (probably contg. the corresponding hydroxy ester); the crude XXIII subjected to a Clemmensen reduction during 26 hrs. gave 4.3 g. unchanged XXIII and 3.2 g. 1-phenyl-4,4-dimethyl-1,2,3,4-tetrahydronaphthalene-2-acetic acid (XXIV), colorless oil. XXIV cyclized as described for XVI yielded 78% 5,5-dimethyl-8-oxo-

5,6,6a,7,8,13-hexahydrobenzo[c]phenanthrene, oil; 2,4-dinitrophenylhydrazone, orange felt-like needles, m. 235-6° (from EtOAc); the ketone hydrogenated catalytically gave 65% pure XIX. IV (2.5 g.) in 50 cc. 1:1 aq. MeOH neutralized with NaOH, the mixt. treated with 0.14 g. NaBH4, and the soln. heated 10 min. to 60°, and decompd. with aq. acid yielded 2.4 g. 4,4-dimethyl-1-hydroxy-1,2,3,4-tetrahydronaphthalene-2-acetic acid (XXV), colorless needles, m. 154-5°. XXV (5.2 g.) in 30 cc. C6H6 added to 1.85 g. **P2O5** in 20 cc. refluxing C6H6, the mixt. refluxed 2 hrs., decompd. with H2O and extd. with H2O, the resulting oil (3.8 g.) refluxed with 30 cc. dil. HCl, the crude product (3.6 g.) from the hydrolysis dissolved in 75 cc. dry C6H6, the soln. treated with stirring with 3.3 g. AlCl3 at 0°, and the complex **stirred** 4 hrs. at room temp. and worked up in the usual manner gave 2.6 g. XXIV. I (30.6 g.) in 125 cc. dry Et2O treated at -70° during 2 hrs. with 0.02 mole PhMgBr in 75 cc. dry Et2O, and the mixt. **stirred** 3 hrs. at -70° and decompd. with satd. aq. NH4Cl yielded 14.6 g. unchanged I and 11 g. CH2:CMeCH2CH(CO2H)CH2Bz (XXVI); XXVI (7.6 g.) treated with CH2N2 gave 4.75 g. Me ester (XXVII), colorless oil, b1.3 147-9°, nD22 1.5188; 2,4-dinitrophenylhydrazone, yellow-orange needles, m. 113-14°. XXVII sapond. and lactonized gave XI; it gave alkylated with C6H6 and then sapond. III in good yield. The ultraviolet absorption spectra of VI and the 5,6-dihydro deriv. of I are recorded.

CC 10 (Organic Chemistry)

L57 ANSWER 14 OF 20 HCA

50:20145 Original Reference No. 50:4189b-i,4190a-i Triterpenoids. XLIII. Constitution of compounds obtained by the dehydration of α-amyrin and related alcohols. Allan, G. G.; Spring, F. S.; Stevenson, Robert; Strachan, W. S. (Roy. Tech. Coll., Glasgow, UK). Journal of the Chemical Society, Abstracts 3371-7 (Unavailable) 1955. CODEN: JCSAAZ. ISSN: 0590-9791.

GI For diagram(s), see printed CA Issue.

AB As a basis for a more systematic nomenclature of the dehydrogenation products here described, the hydrocarbon C27H46 (A), having the constitution and stereochemistry represented is called novursane. In the detn. of the constitution of a no. of products obtained by the dehydration of α-amyrin (I) and related compds. the treatment of 3β-hydroxyurs-12-en-11-one (II) with PCl5 gave 60% 8,10,14-trimethyl-5ξ-novursa-3(4),12-dien-11-one (III) ("α-amyradienone-I"), m. 197-9°, [α]D 167° (c 2.9), and 10% 8,10,14-trimethylnovursa-3(5),12-dien-11-one (IV) ("α-amyradienone-II"), m. 155-6°, [α]D 147° (c 0.8). IV (0.3 g.) was also formed by refluxing 0.5 g. III in 50 cc. AcOH contg. 5 cc. concd. HCl 16 hrs. with addn. of 2 cc. concd. HCl every 4 hrs. A mixt. of 800 mg. III and NaOMe

(from 1 g. Na) in 15 cc. MeOH and 5 cc. 100% H2NNH2.H2O was autoclaved at 200° 15 hrs., the product taken up in 100 cc. petr. ether, chromatographed on Al2O3, eluted with petr. ether and crystd. from MeOH to yield 310 mg. prisms of 8,10,14-trimethyl-5ξ-novaursa-3(4),12-diene (V), m. 134-5°, [α]D 109° (c 1.3), identical with "d-α-amyradiene" (Vesterberg and Westerlind, C.A. 16, 3642), obtained by PCl5, dehydration of I. V (1.0 g.) in 200 cc. CHCl3 was treated with 2 moles O3 at -35°, the mixt. **stirred** at room temp. with 3 g. Zn dust and 50 cc. AcOH 1 hr., the filtered soln. washed with five 250-cc. portions H2O, the CHCl3 evapd. and the residue crystd. from MeOH. Fractional crystn. from MeOH yielded 350 mg. product, which, chromatographed on Al2O3, eluted with petr. ether and recrystd. from MeOH, yielded 250 mg. needles of VI, C27H42O, m. 146-8°, [α]D 210°, unchanged after 2.5 hrs. refluxing with 5% KOH in EtOH. Further elution with petr. ether-benzene (2:1) and crystn. from MeOH gave a small amt. of VII, C27H42O2, m. 204-6°, [α]D 184°. Distn. of the H2O washings yielded acetone, identified as the dinitrophenylhydrazone, m. 121-4°. Treatment of 700 mg. V in 7 cc. CHCl3 with 700 mg. Cl3CCO2H at room temp. for 1 hr. and recrystn. from acetone gave 200 mg. **hexagonal** prisms of 8,10,14-trimethylnovursa-3(5),12-diene (VIII), m. 70-2°, [α]D 123° (c 1.4), λ 2080 A. (ε 4500). VIII was also formed by the Wolff-Kishner reduction of IV by which its structure is established. The infrared absorption spectrum of VI includes a strong band at 1740 cm. -1 (in CCl4) and, consequently, VI contains a CO group in a 5-membered ring. It also gives a yellow color with C(NO2)4 and is recovered unchanged after treatment with alkali, suggesting that the rings A and B are fused in the more stable form. The change in [M]D (+450°) accompanying the conversion of I into VI is in agreement with values observed for comparable reactions, proving that the ring fusion is cis-β. Treatment of II with HI in AcOH (Ewen, et al., C.A. 38, 2028.4) gave 5,8,14-trimethylnovursa-9(10),12-dien-11-one (IX), m. 170-1°, [α]D 171° (c 3.3), λ 2040, 2580, 2900 A. (ε 9900, 11,000, 10,200), yellow color with C(NO2)4. The ultraviolet absorption spectrum of IX ("α-amyradienone-III") closely resembles that of 12-oxooleana-9(11),13(18)-dien-3β-yl acetate (X) and 12-oxoursa-9(11),13(18)-dien-3β-yl acetate (XI), the characteristic absorption spectra of which have been related to the geometry of the C:CC-(O)C:C chromophore. The constitution thus assigned to IX is confirmed by its formation from IV. IV (2 g.) in 10 cc. glacial AcOH was treated with 5 cc. HI (d. 1.7) and refluxed for 8 hrs. Crystn. from MeOH gave 1.2 g. laminas of IX. Wolff-Kishner reduction or refluxing with LiAlH4 in Et2O converted IX into 5,8,14-trimethylnovursa-9(10),12-diene (XII), m. 98-9°, [α]D 120° (c 2.8), λ 2080 A.

(ε 13,200), orange color with $C(NO_2)_4$. This behavior of IX is similar to that of X. Catalytic hydrogenation of 600 mg. IX in 100 cc. AcOH in the presence of Pt (from 250 mg. PtO_2) 24 hrs. and crystn. of the reduction product from acetone-MeOH gave 350 mg. plates of 5,8,14-trimethyl-9ξ,10ξ-novurs-12-ene (XIII), m. 95-6°, [α]D 140° (c 1.4), λ 2060 A.
(ε 2750), yellow color with $C(NO_2)_4$. IX differs from X and XI in its reduction to the monoethylenic hydrocarbon XIII whereas X and XI undergo catalytic hydrogenolysis to the corresponding nonconjugated diene. XII (150 mg.) in 5 cc. $CHCl_3$ and 50 cc. AcOH contg. 10 cc. concd. HCl was refluxed 16 hrs. with the addn. of 2 cc. concd. HCl every 2 hrs. Crystn. of the product from $CHCl_3$-MeOH gave 50 mg. "l-α-amyradiene" (C.A. 38, 2028.4), m. 193-4°, [α]D -110° (c 1.9), λ 2360, 2410, 2500 A. (ε 13,200, 14,500, 8550), also prepd. from V by treatment with BF_3 in AcOH and previously by V. and W. (loc. cit.) by dehydration of I with **P_2O_5**. According to Ewen, et al. (C.A. 38, 2028.4), dehydration of ursa-9(11),12-dien-3β-ol (XIIIa) with PCl_5 gives a dichloro-α-amyradiene, which with Zn yields "d-α-amyratriene" (XIV) whose ultraviolet absorption spectrum shows that the new unsatd. bond is remote from the conjugated system in ring C. XIIIa (3.0 g.) in 80 cc. petr. ether (b. 60-80°) was shaken with 1.47 g. PCl_5 1.5 hrs. and refluxed 2 min. Crystn. of the product from MeOH-$CHCl_3$ gave XIV, m. 132-4°, [α]D 439° (c 0.9), λ 2780 A.
(ε 9500). The constitution of XIV was established by its formation from III. III (500 mg.) in 200 cc. Et_2O was refluxed with 500 mg. $LiAlH_4$ 3 hrs., the crude product in 50 cc. pyridine was refluxed 15 hrs. with 20 cc. $POCl_3$, and the product crystd. from MeOH produced 200 mg. needles of XIV, 8,10,14-trimethyl-5ξ-novursa-3(4),9(11),12-triene. IX (1.0 g.) in 200 cc. anhyd. Et_2O was kept at 0° in the presence of $LiAlH_4$ 72 hrs., and the product isolated in the absence of traces of mineral acid and crystd. from MeOH to yield 5,8,14-trimethylnovursa-1(10),9(11),12-triene (XV), m. 145-6°, [α]D -358° (c 1.6), λ 3200 A. (ε 15,000), similar optically to ergosta-5,7,14,22-tetraen-3β-yl acetate. Treatment of XV with HCl in AcOH and crystn. from MeOH gave needles of 5,8,14-trimethylnovursa-9(10),11,13(18)-triene (XVI), m. 140-2°, [α]D -450° (c 0.5), λ 2860, 2950, 3080 A. (ε 28,200, 33,800, 24,500), previously obtained by dehydration of XIIIa by **P_2O_5**. Ergosta-4,6,8(14),22-tetraene, which contains a chromophore comparable with that in XVI, has similar absorption. The calcd. value (2940 A.) for the position of the absorption max. in XVI, on the basis of Woodward's empirical rules, is in excellent agreement with the observed value.

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49:32158 Original Reference No. 49:6126h-i,6127a-i,6128a-h Preparation and properties of 3,5-di-O-benzoyl-1,2-O-(α-hydroxybenzylidene)-α-D-ribose, and the orthobenzoic acid derivative of D-ribofuranose. Ness, Robert K.; Fletcher, Hewitt G., Jr. (Natl. Inst. of Health, Bethesda, MD). Journal of the American Chemical Society, 76, 1663-7 (Unavailable) 1954. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 49:32158.

AB The hydrolysis of tri-O-benzoyl-β-D-ribofuranosyl bromide (I) gave the previously reported 2,3,5-tri-O-benzoyl-β-D-ribose (II) (cf. C.A. 49, 3024f), together with a new, cryst. isomer (III). III, which is stable to dil. acids, is readily isomerized by aq. pyridine to II. The synthesis of III through the hydrogenolysis of amorphous 3,5-di-O-benzoyl-1,2-O-(α-benzyloxybenzylidene)-α-D-ribose (IV) indicates that it is most probably 3,5-di-O-benzoyl-1,2-O-(α-hydroxybenzylidene)-α-D-ribose (V). III with HBr afforded a cryst., highly reactive 3,5-di-O-benzoyl-D-ribofuranosyl bromide (VI) which on hydrolysis gave amorphous 3,5-di-O-benzoyl-D-ribose (VII). The successive oxidation, reduction, deacetylation, and benzoylation of VII led to erythritol tetrabenzoate (VIII). The treatment of either III or VI with ZnCl2 in Ac2O gave a cryst. 1,2-di-O-acetyl-3,5-di-O-benzoyl-D-ribose (IX). With HBr IX gave an amorphous bromide yielding on hydrolysis a cryst. substance which appeared to be 3,5-di-O-benzoyl-1,2-O-(α-hydroxyethylidene)-α-D-ribose (X), an orthoacetic acid deriv. Ortho acid derivs., a relatively rare type of substance, are briefly discussed. II (10.11 g.) in 30 cc. CH2Cl2 and 3.5 cc. Ac2O treated with 10 cc. 32% HBr in glacial AcOH, the mixt. allowed to stand 6 min. at 20°, poured into a mixt. of ice water and CH2Cl2, the org. layer quickly washed with cold aq. NaHCO3, dried with Na2SO4, filtered through C, concd. in vacuo at about 35°, the resulting crude frothy mass dissolved in 40 cc. Me2CO and 2 cc. H2O, the soln. let stand 75 min. at room temp., treated with CH2Cl2, the mixt. washed with cold. aq. NaHCO3, dried with Na2SO4, evapd. in vacuo at 30°, and the semicryst. residue treated with 70 cc. Et2O and 35 cc. pentane yielded 5.10 g. (50%) practically pure V, m. 142-3°, [α]D 86° (c 0.93, CHCl3), recrystg. from 2:1 Me2CO-H2O in fine needles, m. 142-3°, [α]D 85.3° (c 0.97, CHCl3); the mother liquor concd. and the resulting sirup recrystd. from Et2O-pentane yielded 32% crude II. Pure D-ribose (5 g.) converted successively to Me D-ribofuranoside, its tribenzoate, and 2,3,5-tri-O-benzoyl-β-D-ribofuranosyl bromide as described previously (loc. cit.), the amorphous bromide dissolved in 60 cc. Me2CO and 3 cc. H2O, the soln. allowed to stand 40 min. at room temp., dild. with CH2Cl2, washed with cold aq. NaHCO3, dried, evapd., and the residual sirup crystd. from 120 cc. Et2O and 60 cc. pentane gave 6.55 g. (43%) V, m. 141-2°; the mother liquor concd., the resulting sirup

dissolved in 60 cc. pyridine and 37 cc. H_2O, and the soln. cooled to -5° gave II-pyridine addn. compd., which, dried in vacuo over H_2SO_4, yielded 5.4 g. II (total yield 78%). II (5.00 g.) in 25 cc. $(CH_2Cl)_2$ over solid Drierite nearly satd. with gaseous HBr, the mixt. kept 65 min. at 0°, filtered, concd. in vacuo at room temp., the resulting thick sirup dissolved in 10 cc. $(CH_2Cl)_2$ and 5 cc. quinoline, the soln. cooled, treated with 2.5 cc. $PhCH_2OH$, allowed to stand 19 hrs. at 0-5°, the mixt. dild. with CH_2Cl_2, poured on ice, and the org. layer washed with cold 3N H_2SO_4 and aq. $NaHCO_3$, dried with Na_2SO_4, and concd. in vacuo, gave 6.5 g. sirupy residue; a sample of the residue showed $[\alpha]D$ 81° (c 4, 49, Ph CH_2OH); with 1 drop HBr in $PhCH_2OH$ the rotation fell to 22° in 2 hrs. [the rotation of benzyl β-D-ribofuranoside tribenzoate is 0.0 ± 0.5° (1 0.5 dm., $PhCH_2OH$)]; the remainder of the sirup (6.46 g.) dissolved in 40 cc. EtOAc, hydrogenated 3 hrs. at room temp. over 5 g. prereduced Pd-C, the mixt. filtered, concd., and the residual sirup crystd. from 25 cc. dry Et_2O gave 1.07 g. (21%) V, m. 141-3°; the material isolated from the mother liquor, recrystd. from CCl_4, yielded 2.59 g. (52%) II, m. 103-7°. V (0.5114 g.) in 25 cc. 18:7 dioxane-H_2O showed a specific rotation of 74°; addn. of 0.016 cc. of about 41% HBr did not change this value during 2 months; a similar soln. having asp. rotation of 73° treated with 2 drops NH_4OH changed in 2 hrs. to 66.7°. II showed a rotation of 67.3° in 18:7 dioxane-H_2O (c 1.01); 1.3 hrs. after the addn. of 2 drops concd. NH_4OH it changed to 67.6°. V (1 g.) in 10 cc. pyridine and 2 cc. H_2O kept 31.5 hrs. at room temp., the soln. cooled to 0°, dild. with 6 cc. H_2O, seeded with 2,3,5-tri-O-benzoyl-D-ribose contg. pyridine of crystn., the mixt. treated with 4 cc. H_2O, and the resulting ppt. dried in vacuo at 40° over **P_2O_5** gave 0.89 g. product, which, recrystd. from 2 cc. abs. EtOH and 3.6 cc. pentane, yielded 0.65 g. (65%) II, m. 102-4°, recrystg. from 2 parts CCl_4 0.60 g. fine needles, m. 106-8°, $[\alpha]D$ 68.7° (c 2.05, $CHCl_3$). V (0.5489 g.) in CH_2Cl_2 (total vol. 15.00 cc.) showed a rotation of 4.66° in a 1.5-dm. tube; a gentle stream of HBr passed over the surface of the soln. in the tube for 30 sec., and the soln. mixed showed the following observed rotations: 2.79° (1.5 min.), 4.63° (2.8 min.), 5.32° (5.7 min.), 4.98 (10 min.); the mixt. concd. in vacuo at 0°, and the resulting semicryst. mass recrystd. from 1 cc. dry Et_2O and 1.1 cc. pentane at 0° gave 0.497 g. (99%) VI, m. 88-91° (decompn.); recrystd. from 11 cc. 3:5:3 $CH_2Cl_2Et_2O$-pentane at -5°, the product (0.260 g.) 104-5° (decompn.), $[\alpha]D$ 96° (3 min.), mutarotating to 27° (60 min.) (c 0.47, abs. EtOH). VI (1.00 g.) **stirred** 40 min. in a cooled mixt. of 10 cc. Me_2CO, 1 cc. H_2O, and 1 g. $AgCO_3$, the mixt. filtered, and the filtrate dried with Na_2SO_4 and concd. in vacuo at 25°, gave a

colorless clear sirup which failed to crystallize; a sample (0.3840 g.) in a little glacial AcOH treated with 50.0 cc. 0.0568N Pb(OAc)4 in glacial AcOH and the mixt. dild. to 100 cc. with glacial AcOH and analyzed after 1, 4, and 22 hrs. by the method of Hockett and McClenahan (C.A. 33, 6803.4) showed the consumption of 0.78 mole oxidant/mole compd.; the remainder of the oxidation mixt. (39.5 cc.) poured into a cold mixt. of 200 cc. CH2Cl2, 200 cc. H2O, 40 g. NaOAc, 2.3 g. KI, and 6 cc. 0.1N aq. Na2S2O3, thoroughly shaken, the org. layer washed with aq. NaHCO3, dried with Na2SO4, concd. in vacuo, the residual sirup dissolved in 8 cc. abs. EtOH, hydrogenated 19 hrs. at 2250 lb. pressure over Raney Ni, the mixt. filtered, the filtrate concd. in vacuo, the residual sirup deacylated in the usual manner with Ba(OMe)2, and the product treated with BzCl in pyridine, worked up in the usual way, and crystd. from Et2O yielded 0.0926 g. (41%) crude VIII, m. 181-6°, which, recrystd. from 1:1 C6H6hexane and then from 1:1 CH2Cl2-abs. EtOH, showed no rotation in CHCl3 (c 1.65, 4 dm.) and m. 189-90°. Fused ZnCl2 (0.45 g.) in 8 cc. Ac2O treated with cooling during 6 min. with 1.0 g. II in portions, the mixt. allowed to stand 20 hrs. at 5° poured into 60 cc. H2O, the pptd. brittle mass dissolved after several hrs. in 3 cc. warm abs. EtOH, and the soln. cooled gave 0.52 g. (54%) IX, sheaves of heavy needles, m. 125-7°, [α]D -3.2° (c 1.49, CHCl3), which, recrystd. from 11 parts abs. EtOH, yielded pure IX, m. 127-8°,[α] -3° (c 0.82, CHCl3). VI (0.1024 g.) in 2.00 cc. Ac2O (observed in a 0.5-dm. tube) mutarotated rapidly [0.53° (2.0 min.), 0.91° (3 min.), 1.12° (5.4 and 13.6 min.)]; the soln. treated after 15 min. with a small amt. of powd. fused ZnCl2 gave an almost instant change of the rotation to 0.31° (1.5 and 5.3 min.); the mixt. poured after 9 min. on ice and the ppt. recrystd. from 0.5 cc. abs. EtOH gave 0.0642 g. (60%) IX, m. 126-7°. II (1.03 g.) in 5 cc. CH2Cl2 and 0.3 cc. Ac2O treated with 7 cc. 32% HBr in glacial AcOH, the mixt. poured after 16 min. into ice and CH2Cl2, the org. layer washed with H2O and aq. NaHCO3, dried with Na2SO4, concd. in vacuo at 30°, and the residual clear sirup crystd. from 5 cc. dry Et2O and about 2.5 cc. pentane gave 0.132 g. (15%) crude X, m. 92-7°, recrystd. twice from 10 cc. warm Et2O, m. 129-30°, [α]D 66.4° (c 1.26). X (0.1217 g.) in 7.2 cc. dioxane dild. to 10.0 cc. with H2O showed in a 1.5-dm. tube at 20° a rotation of 1.13°; 1 drop 41% HBr added changed it in 16 hrs. to 1.03°; with 0.15 cc. added pyridine it changed more rapidly: 0.99° (3 min.), 0.79° (7 hrs.), 0.48° (24 hrs.), 0.40° (31 hrs.), 0.32° (48 hrs., const.). IX (1.00 g.) in 10.0 cc. (CH2Cl)2 showed a rotation of -0.37° in a 1.5-dm. tube; 0.24 cc. added Ac2O changed it to -0.36°; with 9.7 cc. 32% HBr in glacial AcOH the following rotations were observed: -1.40° (1.0 min.), -0.05° (1.4 min.), 1.21° (3.5 min.), 1.24° (12

min.). The mixt. poured after 18 min. into ice water and CH_2Cl_2, the org. layer washed with aq. $NaHCO_3$ and H_2O, dried with Na_2SO_4, concd. in vacuo at 35°, and the resulting thick sirup recrystd. from 2 cc. Et_2O gave 0.188 g. crude X, m. 115-18°; a 2nd crop of 0.063 g., m. 115-19°, raised the yield to 28%; the crude X recrystd. from 1:1:1 CH_2Cl_2-Et_2O-pentane and then from 2:1 Et_2O-pentane yielded 0.084 g. pure X, needles, m. 127-8°, $[\alpha]D$ 68.2° (c 0.33, $CHCl_3$); recrystd. again from Et_2O, m. 128-9°; a 2nd recrystn. from CH_2Cl_2-pentane gave a product which showed a double m.p. at 105-6° and 127-8°. Pure β-D-ribofuranose tetrabenzoate (0.4175 g.) in 4.0 cc. Ac_2O treated at 20° with 1 cc. of a soln. of 2.0 g. fused $ZnCl_2$ in 10 cc. Ac_2O, the mixt. poured on ice after the mutarotation ceased (4 hrs.), and the ppt. gum crystd. from abs. EtOH gave 0.2084 g. (56%) 1-O-acetyl-2,3,5-tri-O-benzoyl-D-ribose, m. 128-9°, recrystg. from 5 cc. abs. EtOH in **hexagonal** micaceous plates, m. 129-30°.

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49:1254 Original Reference No. 49:268i,269a-i,270a-i,271a-i,272a-i,273a-i,274a-i,275a-f Terramycin. X. The structure of Terramycin. Hochstein, F. A.; Stephens, C. R.; Conover, L. H.; Regna, P. P.; Pasternack, R.; Gordon, P. N.; Pilgrim, F. J.; Brunings, K. J.; Woodward, R. B. (Harvard Univ.). Journal of the American Chemical Society, 75, 5455-75 (Unavailable) 1953. CODEN: JACSAT. ISSN: 0002-7863.

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 48, 10712b. The antibiotic Terramycin (I) has been shown to have the structure II; the stereochem. assignments in this structural formula are tentative. Anhyd. II was recrystd. twice from PhMe, the resulting purified material (1.8 g.) dissolved in 2 l. dry PhMe, the soln. refluxed 2 h. through a Soxhlet extractor charged with CaH_2, the hot soln. filtered and cooled, and the cryst. deposit dried to const. wt. at 100°/0.1 mm. to give pure I (4-dimethylamino-1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,10,12,12a-hexahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamide), pale yellow crystals, m. 184.5-5.5° (decompn.) (placed in a bath at 175° and heated at 2°/min.), $[\alpha]D25$ -197° at equil. (0.1N HCl); gave pos. $FeCl_3$, Pauly, Friedel-Crafts, Fehling, and Molisch tests; contained 7.8 mol active H/mol; λmax. 245 (4.20), 357 (4.10) in HCl-EtOH, 245 (4.20), 266 (4.14), 380 mμ (log ε 4.16) in EtOH-NaOH; acid consts. of I hydrochloride 3.49, 7.55, 9.24 in H_2O; the apparent pKa of I shifts to 8.0 and 9.8 in 1:1 $HCONMe_2$-H_2O. I in Me_2CO or H_2O was oxidized by several moles $KMnO_4$, but yielded no readily identified products other than NH_3 and Et_2NH. I.HCl in H_2O consumed 8 equivs. HIO_4 within 2 h. at 25°; the hypoiodite oxidn. of I

yielded 1.75 equivs. CHI_3; the oxidn. of I in hot 15% HNO_3 yielded 1.3 equivs. $(CO_2H)_2$, and smaller amts. of an unidentified nitrated phenolic acid, m. 217.5-18.5°. CH_2N_2 (6 g.) in 300 cc. dry Et_2O added to 18.6 g. anhyd. I in 400 cc. dry dioxane at 10°, the soln. let stand 1.5 h. and dild. with 1400 cc. com. hexane, the amorphous ppt. (16.9 g.) dried in vacuo and **stirred** 0.5 h. with 100 cc. MeOH, and the resulting cryst. ppt. recrystd. from 50% aq. MeOH yielded 2.0 g. (10%) dimethylterramycin (III), decomp. without melting at 225°, insol. in H_2O, pyridine, and the common org. solvents, λmax. 272 (4.40), 352 mμ (log ε 4.0). III dissolved in HCl in MeOH, the soln. dild. with Et_2O, and the ppt. carefully recrystd. from EtOAc-MeOH contg. HCl gave III.HCl, yellow **hexagonal** plates, decompd. without melting at 175°, $[\alpha]D28$ -110° (MeOH); pKa 7.7 in aq. $HCONMe_2$. An amorphous unstable material which evolved Me_3N on mild alkali treatment was obtained in 70% yield in the prepn. of III. Anhyd. I (10 g.) in 200 cc. dry dioxane made up with Ac_2O to 1 l., the mixt. let stand 14 days at 25-30°, evapd. to dryness in vacuo below 35°, and the cryst. residue recrystd. twice from PhMe yielded 8.8 g. (75%) 5,12a-di-Ac deriv. of I, m. 208-13° (decompn.), $[\alpha]D25$ 211° (Me_2CO); pKa 6.75 and 8.85 in aq. $HCONMe_2$; gave treated 5 min. at 25° with N NaOH I. I.HCl (2.5 g.) in 7 cc. pyridine treated at 5° with 3.6 g. $PhSO_2Cl$, the mixt. let stand overnight at 5° and poured into 50 cc. Et_2O, the gummy ppt. **stirred** 1 h. with 25 cc. H_2O, and the resulting light tan cryst. solid recrystd. twice from $HCONMe_2$, washed with Me_2CO, and dried 3 h. in vacuo at 100° gave benzenesulfonylterramycinonitrile (10-benzenesulfonoxy-4-dimethylamino-1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,12,12a-pentahydroxy-6-methyl-1,11-dioxo-2-naphthacenenitrile) (IV) contg. 1 mol $HCONMe_2$, m. 210-11°; pKa 6.95; $[\alpha]D25$ -378° ($HCONMe_2$); λmax. 275 (4.23), 342 mμ (log ε 4.06) in acid MeOH; this with Ac_2O-pyridine gave a solid which was recrystd. from EtOH to yield a triacetate crystg. with 0.5 mol H_2O and 0.5 mol EtOH, $[\alpha]D25$ 8° ($HCONMe_2$), pKa 5.3. Terranaphthol (3-hydroxymethyl-4-methyl-1,8-naphthalenediol) (V) was prepd. as previously described (C.A. 48, 2020d) and purified through the triacetate, m. 148.7-9.4°, to give pure V, m. 172.4-3.0°; it gave a green color with alc. or aq. $FeCl_3$ and a red ppt. with aminoantipyrine; λmax. 232 (4.79), 312-341 mμ (log ε 3.89); pKa 7.5; it gave with peroxide, HNO_3, or $K_2Cr_2O_7$ in AcOH intractable tars and was not attacked by Ag_2O in Et_2O. V in dioxane added to 5 mol CH_2N_2 in Et_2O, and the mixt. let stand overnight at 25° gave a mono-Me ether, b0.05 160°, which crystd. slowly from C_6H_6-ligroine and from Et_2O-ligroine to give 25% solid product, m. 88-91°. V (40.8 mg.) in 2 cc. abs. EtOH added to 5 cc. 0.5M aq. H_3BO_3, showed pH 2.20, whereas the blank from 5 cc. H_3BO_3 and 2 cc. EtOH had pH 5.00;

the change in the pH is partly caused by the natural acidity of the added V. V (0.2 g.) ground in a mortar with 2 g. NaOH and 2 g. KOH, the mixt. heated in a Ni crucible 15 min. at 260-70°, the brown melt cooled, dissolved in 15 cc. H2O, quickly acidified with cooling with 4N H2SO4 to pH 1, and dild. to 30 cc., and the insol. crystals and tar filtered off, dried, and recrystd. 3 times with C from hot H2O and from aq. MeOH yielded 0.06 g. terranaphthoic acid (1,8-dihydroxy-4-methyl-3-naphthoic acid (VI), yellow tan crystals, m. 233-5° with some decompn. above 220° when placed in a bath at 200° and heated at 2°/min.; pKa 5.5 and 7.8; λmax. 3.2, 5.85 μ; λmax. 236 (4.60), 310 (3.76), 343 mμ (log ε 3.71); gave a red aminoantipyrine test and a green color with aq. or alc. FeCl3; gave on decarboxylation in boiling quinoline with Cu bronze catalyst 0.35 mol CO2. VI (0.05 g.) in 0.5 cc. dioxane and 0.5 cc. Et2O treated at 0° with 0.05 g. CH2N2 in 10 cc. Et2O, the mixt. let stand overnight at room temp., and the resulting oily product sublimed and crystd. 3 times from MeOH gave the Me ether Me ester of V, pale yellow needles, m. 101-2° (dried at 80°/0.1 mm.), insol. in aq. NaHCO3, did not give a color with FeCl3; λmax. 3.0, 5.83 μ. 1,8-Dihydroxy-2-naphthaldehyde (VII), m. 137.8-8.5°, was obtained in 6% yield by the method of Morgan and Vining (C.A. 15, 1503) and purified by extn. with cyclohexane in a Soxhlet app., recrystn. from cyclohexane, and sublimation at 135°/0.1 mm.; pKa 4.5; λmax. 2.9, 6.15 μ; λmax. 265 (4.53), 324 (3.50), 420 mμ (log ε 4.00). VII (0.15 g.) fused 3 min. at 220° with 0.7 g. NaOH and 0.7 g. KOH, the melt dissolved in H2O, cooled, acidified, the amorphous ppt. filtered off, recrystd. from aq. EtOH and twice from PhMe yielded 40 mg. 1,8,2-(HO)2C10H5CO2H, colorless crystals, m. 170.5-1.5 with vigorous gassing; pKa 3.2 and above 12; λmax. 6.05 μ in dioxane; λmax. 245 (4.72), 314 (3.67), 360 (3.94), 372 mμ (log ε 3.91); was decarboxylated in excellent yield to 1,8-C10H6(OH)2 when heated to 125°/0.05 mm. Alkali fusion of 4,5,1-(HO)2C10H6CHO gave 1,8,4-(HO)2C10H5CO2H, m. 58-60° (decompn.); pKa 5.6 and 8.2; it underwent rapid decarboxylation in vacuo at 130°; λmax. 220 (4.44), 335 mμ (log ε 4.00). Zn dust washed with 0.1N HCl and then with EtOH, dried at 25° in vacuo, heated 15 min. in a slow H stream at 300°, and cooled under H gave purified Zn dust. V (100 mg.) mixed with 5 g. purified Zn dust, the mixt. heated in a Pyrex tube in a slow stream of N to near the softening point of the glass, and the alkali-insol. viscous green oil condensing in the cooled parts of the tube distd. gave 7.8 mg. (10%) 1,3-C10H6Me2, b0.1 80°, m. -10 to -8°; picrate, m. 116.5-18.5°; styphnate, m. 118-20°; C6H3(NO2)3 adduct, m. 134-6°. VI (75 g.) mixed with 7.5 g. purified Zn dust, the mixt. heated in a H stream, the crude product (18 mg.) dissolved in 0.5 cc. CS2, and the soln.

washed with 10% aq. NaOH and distd. gave a mixt. contg. about 70% 1-C10H7Me (VIII) and lesser quantities 2-C10H7Me (IX) and C10H8. VIII distd. similarly with Zn dust gave small amts. of IX and C10H8, while IX yielded only traces of C10H8. The NaOH-Zn degrdn. of 100 g. I as described previously, the resulting NaHCO3-sol. fraction distd. at 220-4°/0.05 mm., and the yellow viscous distillate (1.8 g.) recrystd. 9 times from cyclohexane gave 1 g. (2%) isodecarboxyterracinoic acid (7-hydroxy-3-methylindanone-2-acetic acid) (X), colorless plates, m. 111.5-12.5°; pKa 5.5 and 9.7; λmax. 225 (4.04), 319 (3.56) in EtOH-HCl, 237 (4.34), 262 (3.94), 363 mμ (log ε 3.96) in EtOH-NaOH; λmax. 5.88, 5.99 μ (CHCl3); gave a purple color with alc. FeCl3. X (150 mg.) treated 2 h. at 0-20° with 75 mg. CH2N2 in 20 cc. Et2O yielded 100 mg. Me ester, nD25 1.5470, gave a purple FeCl3 test. X reacts readily with 2 g.-atoms Br in glacial AcOH to yield HBr and an oily product, presumably the 2-Br deriv. of X which gave refluxed in N alkali a cryst. Br-free solid, insol. in aq. NaHCO3 and giving a violet FeCl3 test. X (140 mg.) fused 8 min. with 2 g. NaOH and 2 g. KOH at 325° yielded 30 mg. solid acid (not further investigated) and 10 mg. m-EtC6H4OH. Freshly sublimed 1,8-C10H6(OH)2 (18 g.) in 75 cc. abs. EtOH hydrogenated at 60° and 50 lbs. pressure over 6 g. Raney Ni yielded 10.9 g. 8-hydroxy deriv. of 1-tetralone (XI), colorless oil, b0.07 82°, nD20 1.5871, λmax. 260 (3.97), 335 mμ (log ε 3.49). Freshly sliced Na (4.2 g.) and 13 g. XI in 35 cc. EtOAc refluxed 4 h. with stirring under dry N, the mixt. cooled, acidified with 5% AcOH and crushed ice, and extd. with seven 100-cc. portions Et2O, the ext. washed with satd. aq. NaHCO3, dried with MgSO4, and evapd., and the oily residue treated with a satd. soln. of Cu(OAc)2 in MeOH yielded 7.8 g. Cu salt (XII) of the 2-Ac deriv. (XIII) of XI, m. 254-5° (decompn.) (from C6H6). A portion of the XII decompd. with 10% H2SO4, the mixt. extd. with Et2O, the ext. washed with NaHCO3, dried, and evapd., and the residue distd. evaporatively at 150°/0.05 mm. gave XIII, λmax. 267 (3.74), 348 mμ (log ε 4.09), λmax. 5.87, 6.25-6.35 μ. I.HCl (15 g.) treated with 15.2 g. dry HCl in 600 cc. dry Me2CO cooled to -5°, the mixt. let stand 11 h. to reach a const. rotation of [α]D20 -300° and dild. with 700 cc. Et2O, and the yellow ppt. (12.9 g.) recrystd. from 250 cc. BuOH-dioxane (1:2) yielded 9.4 g. (50%) pure acetonylanhydroterramycin (XIV) hydrochloride, decompd. at 225° without melting, [α]D20 -455° (MeOH), pKa 3.8, 5.5, and 7.2; the absence of the Me2CO carbonyl band in the IR spectrum, together with the rapid elimination of Me2CO in acid or basic soln. led to the conclusion that the Me2CO is bonded to the amide N in XIV; in alk. EtOH, the UV spectrum undergoes a rapid reversible change to a stable curve which is identical with that of a mixt. of apoterramycins. The distn. of an aq. soln. of XIV gave

Me2CO, identified as the 2,4-dinitrophenylhydrazone, m. 126-7°. XIV (4 g.) in 20 cc. H2O adjusted rapidly with 5% aq. NaHCO3 to pH 5, and the amorphous ppt. recrystd. from Me2CO gave anhydroterramycin as an acetone solvate, m. 180-90° (decompn.) (dried at 100°/0.1 mm.), [α]D25 52° (from 1:1 MeOH-dioxane); it gave a green color with FeCl3, a red-green color with HNO2, and an intensive blue color with dil. Br solns.; λmax. 271 (4.56), 425 mμ (log ε 3.80) in acid EtOH, λmax.Nujol 5.83 μ. 1,8-Dihydroxyanthraquinone (3 g.), m. 193-4°, in 50 cc. 4% aq. NaOH hydrogenated 2.5 h. over 1 g. 5% Pd-C, the mixt. filtered rapidly into excess dil. HCl, and the cryst. ppt. recrystd. with C from aq. Me2CO yielded 1.2 g. 8,9,10-trihydroxy-1-oxo-1,2,3,4-tetrahydroanthracene, m. 180-2°, and 0.5 g. 2nd crop, m. 164-7°; anal. sample, red needles, m. 186-8°; pKa 8.3; λmax. 267 (4.55), 425 mμ (3.83) in acid MeOH, λmax. 3.0, 6.15 μ. IV in anhyd. Me2CO-HCl let stand overnight at 5°, the soln. dild. with Et2O, and the cryst. ppt. recrystd. twice from HCONMe2-EtOH and dried at 100°/0.1 mm. over **P2O5** gave benzenesulfonylanhydroterramycinonitrile (10-benzenesulfonoxy-4-dimethylamino-1,4,4a,5,12,12a-hexahydro-3,5,11,12a-tetrahydroxy-6-methyl-1,12-dioxo-2-naphthacenenitrile), yellow prisms, [α]D25 -390° (HCONMe2); pKa 6.3; λmax. 275 (4.58), 400 mμ (log ε 3.88). I.HCl (50 g.) in 100 cc. 0.5N HCl heated 9 h. at 60°, the clear yellow soln. dild. to 375 cc. and adjusted with 10% aq. NaOH to pH 3.5, the amorphous filtrate of α- (XV) and β-apoterramycin(3-[(4-carbamoyl-2-dimethylamino-3,6-dihydroxy-5-oxo-3-cyclohexen-1-yl)hydroxymethyl]-1,8-dihydroxy-4-methyl-2-naphthoic acid γ-lactone) (XVI) filtered off, washed with H2O, and dissolved in 500 cc. hot EtOH, the soln. let stand 24 h., the solid deposit filtered off, suspended in 50 cc. H2O, and dissolved by the addn. of 12N HCl to pH 1, the soln. filtered and concd. in vacuo, the residual sirup let stand 24 h., the cryst. HCl salt filtered off, washed with ice-cold 6N HCl, and dissolved in H2O, the soln. adjusted to pH 3.5, and the ppt. recrystd. from EtOH gave 16 g. pure XV, m. 190-200° (decompn.)(dried 3 h. at 100°/0.1 mm.), [α]D25 -45° (HCONMe2); λmax. 250 (4.77), 377 mμ (log ε 3.87) in acid EtOH, λmax.dioxane 5.82 μ; HCl salt, m. 180-95° (decompn.) (dried at 80°/10 mm. in dry HCl), [α]D25 123° (EtOH); pKa 4.0, 5.1, and 8.4; λmax.Nujol 5.75-5.85 μ. The filtrate from the first recrystn. of the XV-XVI mixt. concd. in vacuo to 100 cc., acidified with 60 cc. 2.5N HCl, and cooled 24 h. to 5° yielded 21 g. XVI HCl salt in 2 crops; the crude salt recrystd. twice by dissolving in hot EtOH and adding 0.4 vols. H2O, and the ppt. dried in a slow stream dry HCl at 50°/5-10 mm. gave pure XVI.HCl, m. 195-205° (decompn.), [α]D25 -28° (EtOH); pKa 3.6, 5.2, and 7.8;

λmax. 248 (4.78), 375 mμ (log ε 4.00); λmax.Nujol 5.70, 6.0 μ (shoulder). XVI was not obtained in cryst. form. XV and XVI are readily interconvertible at pH 1 and 8. XVI.HCl formed an extremely stable solvate with MeOH which is not removed on prolonged drying at 100° in vacuo. XVI.HCl (1.0 g.) in 2.5 cc. pyridine and 2.5 cc. Ac2O heated 1.5 h. at 100°, the mixt. poured on ice, the amorphous ppt. filtered off, washed with H2O, dried in vacuo over CaCl2, and dissolved in 150 cc. dry Et2O, and the soln. treated with dry HCl gave 0.5 g. ppt. which yielded recrystd. twice from 5 cc. MeOH 0.10 g. pure tri-Ac deriv. of XVI.HCl crystg. with 0.5 mol H2O, m. 201.5-2.5° (decompn.) (dried 2 h. at 80°/0.1 mm.); pKa 3.4 and 7.2. The presence of small quantities of XV and XVI in the presence of large amts. of I or terrinolide is readily demonstrated by paper chromatog. in a descending system with 5:4:1 H2O-BuOH-AcOH showing the following Rf values: I 0.42, XV 0.21, XVI 0.74, and terrinolide 0.91; all 4 compds. show fluorescence under UV light. In this manner, as little as 1% XVI could be detected in XV. XV (4 g.), 20 g. NaOH, and 30 g. KOH powd. in a mortar fused 10 min. at 240°, the melt cooled, dissolved in 400 cc. ice and H2O, acidified with 6N H2SO4 to pH 2, and extd. with five 150-cc. portions Et2O, the ext. dried with CaCl2 and concd. to about 5 cc. on a steam bath, the cryst. deposit filtered off, washed with a few cc. cold dioxane, and combined with a 2nd crop crystals which pptd. from the mother liquor, and the total product (0.42 g.) sublimed at 125°/0.02 mm. yielded 50 mg. red crystals which were resublimed, recrystd. twice from hot dioxane, and sublimed again to give 22 mg. pure 2,5-dihydroxybenzoquinone, λmax. 285 mμ (log ε 4.27) in acid-EtOH, λmax. 6.05, 61.4 μ; di-Ac deriv., m. 159-60°; the residue from the sublimation of the crude fusion product recrystd. 3 times from dioxane gave 20 mg. relatively insol. yellow product, aparently a mixt. of 4,5-dihydroxy-1-methyl-2,3-naphthalenedicarboxylic acid and its anhydride, m. 260-70° (with prior decompn.), λmax. 5.47, 5.57, 5.80, 6.12 μ; gave heated with aq. dioxane substantial amts. VI; the mother liquors from the acid-anhydride mixt. recrystd. from dioxane and then from aq. MeOH yielded 100 mg. pure VI, m. 235° (decompn.). IV (5 g.) in 50 cc. MeOH satd. at 0° with dry HCl, the mixt. heated 1 h. at 60°, and the colorless cryst. ppt. which appeared to be a half-HCl salt dried (3.2 g.) and recrystd. from HCONMe2EtOH-H2O yielded benzenesulfonylapoterramycinonitrile [3-(4-cyano-2-dimethylamino-3,6-dihydroxy-5-oxo-3-cyclohexene 1-yl)hydroxymethyl-8-benzenesulfonoxy-1-hydroxy-4-methyl-2-naphthoic acid γ-lactone] monohydrate, rectangular plates, [α]D25 29° (HCONMe2), pKa 5.7 and 8.5; λmax.Nujol 5.75 μ. I.HCl (50 g.) in 100 cc. 0.5N HCl heated at 60° and aerated 9 days at the rate of 2 cc./min., the solid deposit filtered off, the filtrate aerated again 5 days,

and the addnl. 7.5 g. solid product combined with the 1st crop recrystd. from aq. iso-PrOH yielded 25 g. crude terrinolide [1,8-dihydroxy-4-methyl-3-(4-carbamoyl-α,2,3,5-tetrahydroxybenzyl)-2-naphthoic acid γ-lactone] (XVII) in 3 crops; an anal. sample was obtained by recrystn. 3 times from MeOH-free Me2CO and drying 5 h. at 100°/0.1 mm., m. 210-15° (decompn.), [α]D25 -16° (1:1 MeOH-0.1N HCl); λmax. 249 (4.75), 360 mμ (log ε 4.08), λmax.Nujol 5.85, 6.05 μ; pKa 4.6 and 7.5; sol. in EtOH, Me2CO, and aq. NaHCO3, insol. in C6H6, Et2O, and H2O; gave a green FeCl3 test, a pos. Wildi catechol test, and a pos. Fehling test; increased the acidity of H3BO3 similarly as 1,8-C10H6(OH)2; formed solvates with H2O and MeOH which were stable at 100°/0.1 mm. for many hrs. XVII was also obtained in comparable yield but slower by heating an acid soln. of I 1-2 mo at 60° in a loosely stoppered flask; small amts. of O are desirable; no XVII was formed under N, while with excess air or O, a tarry intractable polymeric product was formed. XVII (1 g.), 0.5 g. dry NaOAc, and 5 cc. Ac2O heated 1 h. on the steam bath, the mixt. cooled, the tan colored cryst. deposit **stirred** into 80 cc. ice-water, and the product filtered off and recrystd. twice from Me2CO-MeOH gave the penta-Ac deriv. (XVIII) of XVII, colorless needles, m. 229-30°, [α]D25 34° (Me2CO), sol. in CHCl3 and Me2CO, slightly sol. in EtOH, gave a neg. FeCl3 test and was only slowly sol. in dil. NH4OH. XVII (3 g.) and 40 cc. MeI in 600 cc. Me2CO refluxed 4 days with 30 g. K2CO3, the hot soln. filtered, dild. with 20 cc. H2O, and concd. in vacuo, and the residual viscous oil washed with H2O, and recrystd. from Me2CO and then from Me2CO-EtOH gave 1.6 g. pure penta-Me deriv. (XIX) of XVII, m. 225-7°, [α]D25 -9.2° (Me2CO), insol. in alkali; λmax. 250 (4.71), 362 mμ (log ε 3.94).

XIX (0.3 g.) refluxed 4 h. with 5 cc. 15% HCl and 25 cc. glacial AcOH, and the solvent removed in vacuo left a mixt. of tri-Me derivs. of XVII; a 0.2 g. portion suspended in 5 cc. 2% aq. NaHCO3 and dissolved with the min. amt. 10% aq. NaOH, the soln. cooled to 0° and treated portionwise with 7.2 cc. 5% aq. KMnO4, the MnO2 dissolved with NaHSO3, the soln. acidified and extd. with Et2O, the ext. concd. to dryness, and the oily residue recrystd. from EtOH and then sublimed at 175°/0.05 mm. yielded 6 mg. 1,8-dimethoxy-4-methylnaphthalene-2,3-dicarboxylic acid, colorless crystals, m. 230-5°, sublimed at 165°; sol. in hot aq. NaOH; λmax. 247 (4.42), 308 (3.79), 338 mμ (3.74), λmax.CHCl3 5.50, 5.67 μ; an aq. soln. acidified did not give the acid, but pptd. the anhydride on heating; gave a neg. FeCl3 test. I hydrochloride (10 g.) in 300 cc. 0.1N HCl refluxed 10 days under N, the partially cryst. brown ppt. recrystd. 4 times from hot HCONMe2, and the resulting colorless crystals (2.5 g.) contg. solvent of crystn. **stirred** 3 days with Et2O and dried at

100°/0.1 mm. gave racemic XVII, white, insol. in the common org. solvents, the UV spectrum was identical with that of (-)-XVII. Racemic XVII in pyridine treated with Ac2O gave the racemic XVIII in a low-melting form, m. 198-200° (decompn.) (from EtOH), which was converted on prolonged heating in EtOH to a relatively insol. stable form, m. 222-3° (decompn.); the 2 forms showed indentical IR spectra in dioxane, but the spectra differed slightly in mull. Racemic XVII methylated 48 h. as described for (-)-XVII yielded the racemic XIX, m. 234.5-5.5°, as well as a tetra-Me ether, m. 238-9°; the 2 ethers were readily sepd. by chromatog. on Florisil with Me2CO; the IR spectra of the 2 XIX in dioxane are identical. XVII (10 g.) refluxed 72 h. under N with 120 cc. 12N H2SO4, the insol. material filtered off, washed free of sulfate with H2O, dried in vacuo (7 g.), dissolved in 150 cc. Me2CO, filtered, and chromatographed on 150 g. acid-washed Florisil, the eluate collected until pale yellow in color and acidified with 100 cc. 2N HCl, the Me2CO removed in vacuo at room temp., and the cryst. residue (3.75 g.) recrystd. from EtOH and then from EtOH-C6H6, and dried at 100°/0.1 mm. yielded 2.5 g. pure racemic decarboxamidoterrinolide [1,8-dihydroxy-4-methyl-3-(α,2,3,5-tetrahydroxybenzyl)-2-naphthoic acid γ-lactone] (XX), decompd. at 215-50° without melting; pKa 4.7, and 10.2; λmax. 247 (4.70), 375 mμ (log ε 4.00), λmax.dioxane 5.75 μ; gave a pos. Wildi test, a pos. aminoantipyrine test, a green color with alc. FeCl3, a deep red color on aeration in NH4OH (reversed by NaHSO3); was susceptible to oxidn. in alkali; sol. in EtOH and Me2CO, insol. in C6H6 and CHCl3; formed a very stable solvate with MeOH; gave on alkali fusion VI. XVI (2 g.) in 100 cc. 12N HCl refluxed 24 h. in a slow stream of O-free N and the amorphous ppt. filtered off (1.1 g.) and recrystd. from Me2CO yielded 1.0 g. (70%) XX. The penta-Me deriv. (XXI) of XX, m. 150-1° (from EtOH), was prepd. as described for XIX, insol. in cold. alc. NaOH, sol. in 10% aq. alc. NaOH on prolonged heating at 120°; acidification of the cooled soln. pptd. the lactone directly. The penta-Ac deriv. of XX, m. 243-5° (decompn.) (from Me2CO-petr. ether), was prepd. as described for XVIII. XX (1 g.) in 15 cc. anhyd. pyridine and 5 g. p-MeC6H4SO2Cl kept 28 h. at 25° the mixt. poured into 125 cc. H2O, and the amorphous ppt. dried, dissolved in 25 cc. Me2CO, and dild. with 25 cc. EtOH (a 2nd crop was obtained on concn.) gave 2.6 g. pure penta-p-toluenesulfonyl deriv. of XX, m. 154-8° (from Me2CO-C6H6 and dried 24 h. at 100°/0.1 mm.). KMnO4 (29 g.) added portionwise during 2 h. with stirring to 3.5 g. XXI in 40 cc. pyridine and 15 cc. H2O at 75°, the mixt. treated with 20 cc. pyridine and 25 cc. H2O, and **stirred** 1 h., the excess KMnO4 destroyed with H2O2, the mixt. concd. in vacuo with repeated addn. of H2O, the aq. suspension filtered and adjusted to pH 2, and the yellow amorphous product recrystd. twice from aq. EtOH gave 0.23

g. decarboxamidoterrinolidic acid pentamethyl ether [1,8-dimethoxy-3-(α-hydroxy-2,3,5-trimethoxybenzyl)naphthalene-2,4-dicarboxylic acid γ-lactone] (XXIIa) or possibly XXII, pale yellow crystals, m. 210-12.5° (dried at 100°/0.1 mm.); λmax. 256 (4.56), 340 mμ (log ε 3.92), λmax.CHCl3 5.75-5.8μ. XXI (1 g.) dissolved in 20 cc. concd. HNO3 at its f.p., the soln. kept 7 days at 30° and then 6 days at 25°, the amorphous ppt. (0.20 g.) filtered off and sublimed at 75°/0.1 mm. to yield 0.10 g. (CO2H)2 and the unsublimed residue recrystd. 4 times from Me2COC6H6 and sublimed at 140°/0.05 mm. yielded 50 mg. pure 3-methoxy-6-methylpyromellitic dianhydride, m. 270-1°; showed in the IR spectrum 4 CO bands of progressively increasing intensity between 5.35 and 5.60 μ, while the Na salt showed only carboxylate ion absorption at 6.30; λmax. 252 (4.19), 400 mμ (log ε 3.90) in concd. H2SO4. XXI (0.42 g.) in 20 cc. THF treated with 20 cc. 0.5M LiAlH4 in Et2O, the mixt. dild. with 150 cc. Et2O, the turbid soln. **stirred** 3 h. at 25° the excess LiAlH4 decompd. carefully with 50 cc. H2O, the aq. layer extd. with three 100-cc. portions Et2O, the combined Et2O solns. dried with CaCl2 and evapd. to dryness, and the residue recrystd. 3 times from Et2O yielded 0.10 g. pure 2-hydroxymethyl-4-methyl-3-(α-hydroxy-2,3,5-trimethoxybenzyl)-1,8-dimethoxynaphthalene (XXIII), m. 114-15°, λmax. 238 (4.85), 292 mμ (log ε 3.94). XXIII (50 mg.) in 1 cc. dioxane contg. 0.05 cc. 6N HCl heated 1.5 h. at 100°, the red soln. evapd. to dryness in vacuo, and the amorphous residue sublimed at 220°/0.1 mm. and recrystd. twice from EtOH yielded 8 mg. 1,3-dihydro-7,8-dimethoxy-4-methyl-3-(2,3,5-trimethoxyphenyl)-naphtho[2,3-c]furan, m. 148.8-50.8°; λmax. 237 (4.87), 292 (3.94), 370 mμ (2.39). Zn dust (50 g.) added portion-wise to 50 g. I.2H2O in 300 cc. glacial AcOH with stirring, the mixt. **stirred** 8 h. at 30° and filtered, the filtrate freeze-dried, the amorphous yellow product dissolved in 300 cc. MeOH contg. 25 cc. concd. HCl, the soln. poured into 500 cc. H2O, the resulting slurry (pH 1) extd. with four 200-cc. portions Et2O, the ext. evapd. to dryness at 10°, and the solid residue sepd. from a little H2O and triturated with Me2CO yielded 11.4 g. (27%) de(dimethylamino)terramycin-[1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,10,12,12a-hexahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamide] (XXIV), pale yellow plates, m. 216-17° (decompn.)(from Et2O and then MeOH-CHCl3), [α]D25 -137° (MeOH), -47° (Me2CO); pKa 6.8 and 8.9; λmax. 261 (4.25), 363 mμ (log ε 4.17). XXIV (0.5 g.) in 10 cc. MeOH and 1 cc. concd. HCl boiled 1 min., the soln. cooled, and the heavy yellow cryst., ppt. filtered off and recrystd. from dioxane-MeOH gave 0.4 g. pure anhydrode(dimethylamino)terramycin (XXV), m. 232-3°

(decompn.), [α]D25 170° (dioxane); the UV spectrum is substantially identical with that of anhyd. XIV in acid or alk. EtOH soln. XXV (0.23 g.) dissolved in 2 cc. 0.5N NaOH under N, and the soln. acidified gave de(dimethylamino)apoterramycin, colorless crystals, recrystd. from HCONMe2MeOH; pKa 4.6 and 8.1; λmax. 251 (4.63), 375 (4.06) in acid EtOH; λmax.Nujol 5.75, 6.05 μ. I, Zn, and AcOH in the proportions used for the prepn. of XXIV **stirred** 4 days at 25-30°, the mixt. filtered, the filtrate concd., the residual viscous sirup **stirred** with 500 cc. H2O, the amorphous ppt. filtered off, washed with H2O, dried, and extd. exhaustively in a Soxhlet app. with Et2O, the ext. evapd. to dryness, and the amorphous residue triturated with Me2CO and then recrystd. from Me2CO yielded 21 g. (50%) de(dimethylamino)deoxyterramycin (1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,10,12-pentahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamide) (XXVI), contg. 0.5 mol Me2CO of crystn., m. 180-1° (decompn.) when placed in a bath at 165° and heated at 2°/min.; prolonged drying at 80° removed only a portion of the Me2CO of crystn.; pKa 7.1 and about 11.5; λmax. 263 (4.31), 320 mμ (log ε 4.22); λmax. 5.80, 6.08; attempted recrystns. from MeOH, CHCl3, AcOH, or dioxane yielded only an amorphous product unless Me2CO was present. XXVI (2 g.) dissolved in 50 cc. 0.5N alc. KOH, the resulting semisolid gel treated after 12 h. dropwise with glacial AcOH, and the resulting granular cryst. ppt. recrystd. twice from AcOH-H2O, and twice from aq. EtOH, and dried 18 h. at 100°/0.1 mm. gave isodeoxyde(dimethylamino)-terramycin [4,4a,5,6,7,8-hexahydro-1,3,5-trihydroxy-6-(7-hydroxy-3-methylphthalidyl)-8-oxo-2-naphthamide (XXVII), decompd. without melting at 210-20°; pKa 7.2 and 9.2; λmax. 242 (4.16), 256 (4.14), 314 mμ (log ε 4.29); λmax. 5.75, 6.15μ. XXVII (100 mg.) heated 5 min. at 0.1-0.5 mm. pressure in a Pyrex tube in a metal bath at 400°, and the volatile material collecting in the cool section of the tube distd. at 100°/0.1 mm. yielded 3.5 mg. 7-hydroxy-3-methylphthalide, m. 108-10° (from H2O). I.2H2O (10 g.) added in portions with stirring to 80 cc. H2SO4 in 30 cc. H2O at 10°, the soln. warmed to room temp., **stirred** overnight under N, and slowly dild. with gentle intermittent stirring with 800 g. clean ice, the resulting mixt. of cryst. and red amorphous products filtered off, washed with H2O and then with Me2CO, dried in vacuo (1.8 g.), suspended in 20 cc. HCONMe2 and filtered, and the filter residue washed with small vols. HCONMe2 and then with 100 cc. Me2CO gave 280 mg. (3%) terrarubein, C22H20N2O6 (XXVIII), red-orange needles, decompd. without melting at 250-60°, λmax. 255 (4.47), 435 mμ (log ε 3.94) in AcOH-dioxane-EtOH; λmax. 5.80, 6.07, 2.9-3.1; sol. in hot HCONMe2 with some decompn.; slightly sol. in glacial AcOH, and virtually insol. in the

other common solvents. XXVI (2.1 g.) in 65 cc. MeOH satd. with HCl let stand 3 h., and the resulting mixt. (1.83 g., 97%) of microcryst. and amorphous product recrystd. twice from HCONMe2 yielded 50% de(dimethylamino)terrarubein (XXIX), charred and decompd. at 200-300° without melting; slightly sol. in hot glacial AcOH, quite sol. in boiling PhNO2 with decompn., virtually insol. in the other common org. solvents except HCONMe2; λmax. 271 (4.41), 315, 355, 450 mμ (log ε 4.00-4.05) in 1:9 AcOH-EtOH; λmax.Nujol 5.93, 6.02 μ; was also obtained by the treatment of XXVI with hot glacial AcOH or hot HCO2H. Purified Zn dust (20 g.) mixed with 200 mg. cryst. XXIX, the mixt. heated to nearly red heat in a slow stream H, the distd. products (6.0 mg.) combined, recrystd. from CHCl and xylene, and sublimed in vacuo at 180-200° yielded pure naphthacene, sublimed without melting at 290°. XXVIII (40 mg.) treated similarly with 3.5 g. purified Zn dust and the crude distillate sublimed twice gave 0.25 mg. pure naphthacene. I treated with strong cold mineral acids yielded small amts. of XVIII which must be a dimethylaminosubstituted XXIX. Zn dust distn. of I gave only a trace of an uninformative hydrocarbon mixt.

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48:60340 Original Reference No. 48:10675e-i,10676a-i,10677a

Stereochemistry of the β-phenylserines: improved preparation of allophenylserine. Shaw, Kenneth N. F.; Fox, Sidney W. (Iowa State Coll., Ames). Journal of the American Chemical Society, 75, 3421-4 (Unavailable) 1953. CODEN: JACSAT. ISSN: 0002-7863.

AB cf. preceding abstr. The prepn. of phenylserine (I) and allo-I (II) by condensation of BzH and H2NCH2CO2H (III) has been studied by the use of paper chromatography. The isomers were prepd. in comparable quantities with a 1-hr. condensation period; the proportion of II decreased sharply with longer reaction time. II forms a hemihydrate, and a poorly sol. addn. compd. with dioxane which was used to sep. II from I. The HCl salts, the Me, Et, Pr, and iso-Pr ester HCl salts, and the corresponding esters of I and II were prepd. Threonine (IV) and allothreonine (V) were sepd. by paper chromatography under the same conditions as I and II. Aq. solns. of I and II were applied to No. 4 Whatman paper, the resulting spots let dry at room temp., the paper stapeled to a cylinder, the upright cylinder placed in 125-50 cc. of the upper H2O-poor layer from a mixt. of 200 cc. BuOH, 150 cc. H2O, 25 cc. Me2CO, and 25 cc. concd. NH4OH, the liquid allowed to ascend 3-6 hrs. at room temp., the solvent front penciled, the cylinder dried in air at room temp., and the opened sheet sprayed uniformly with 0.2% ninhydrin soln. in BuOH satd. with H2O and dried 10-15 min. at 80° to give orange-brown spots which darkened to violet within 24 hrs. A similar paper chromatogram of spots of 0.1% aq. solns. of IV and V

(5.5 hrs. ascent) gave with ninhydrin blue-violet spots showing Rf values of 0.18-0.19 and 0.13-0.14, resp. III (30.0 g.) and 24.0 g. NaOH in 100 cc. H2O treated with cooling to 15° and rapid stirring with 84.9 g. BzH in 1 portion, the condensation cake let stand different periods of time with various batches, treated dropwise at 15° during 0.5 hr. with 50.0 cc. concd. HCl, the mixt. **stirred** 1 hr., filtered, the filter cake thoroughly mixed with three 200-50-cc. portions of boiling 95% EtOH, the resulting slurry filtered each time, and the washed product dried to const. wt. over Anhydrone at 50-60° and 10-15 mm. gave a mixt. of I and II the proportions of which were detd. by paper chromatography. In two 1-hr. runs acidification of the mixt. gave a thin slurry; further agitation caused thickening to a smooth paste and then to large lumps; the clear pale yellow supernatant, contg. only a few cc. BzH, was cooled 2 hrs. to 5°, filtered off, and the solid filter residue sucked dry and worked up further as described to give 33.4 g. (46%) mixt. contg. 55-60% I and 40-5% II; from the aq. filtrate and EtOH washings was recovered 15-25% III. Three batches acidified after 4 hrs. thickened to a stiff paste which was refrigerated 1-24 hrs. at 5°, suctiondried, the filter cake **stirred** with 100 cc. boiling EtOH, the resulting solid cake slurried with 150 cc. boiling EtOH, filtered, and the product treated in the usual manner to give 44.3 g. (61%) mixt. contg. 80-5% I and 15-20% II; 5-10% III was recovered. With a condensation time of 24 hrs., 52.7 g. (73%) I was the only reaction product, with a recovery of 2-4% III. In a similar 60-hr. run the yield of the exclusively formed I was 49.0 g. (68%), with 1-2% III recovered. I (2.500 g.) dissolved in 30 cc. boiling H2O, and the soln. dild. with 30 cc. boiling EtOH gave 2.175 g. I.H2O, layered **hexagonal** plates (dried 18 hrs. over Anhydrone at 50-60° and about 20 mm. pressure). II (2.500 g.) in 35 cc. boiling H2O dild. with 35 cc. boiling dioxane, the mixt. refrigerated overnight at 5°, filtered, and the filter residue washed with cold 50% aq. dioxane and dried in air at room temp. gave 2.998 g. (97%) II-dioxane adduct (VI) after drying, unchanged by heating 2 hrs. at 77° and about 0.1 mm. over **P2O5**. VI (11.124 g.) in 100 cc. boiling H2O gently simmered 5-10 min., the vessel scratched with cooling, and the resulting 5.972 g. (63%) II.0.5H2O, **hexagonal** microprisms, recrystd. from hot H2O, washed with ice H2O, and dried in air at room temp. gave the pure hemihydrate; slow evapn. of aq. II at room temp. gave also the hemihydrate; the filtrate from the crude II.0.5H2O heated to boiling and dild. with an equal vol. of boiling dioxane gave 2.856 g. (26% recovery) VI. II (2.500 g.) in 50 cc. hot H2O dild. with 50 cc. boiling Me2CO, the soln. refrigerated overnight at 5°, filtered, and the residue washed with 50% aq. Me2CO, Me2CO, and Et2O, and dried 12 hrs. at 50-60° and 10-15 mm. over Anhydrone yielded 1.818 g. (73% recovery) anhyd. II, long

fibrous needles; recrystn. from hot H_2O alone yielded anhyd. II also, if the soln. was let cool slowly at room temp. with frequent swirling. The crude product from a 1-hr. condensation of BzH and III contg. 55-60% I and 40-5% II (89.2 g.), recrystd. from 890 cc. boiling H_2O, gave 26.7 g. (30% recovery) I contg. less than 5% II; the aq. filtrate heated to boiling and dild. with an equal vol. of dioxane pptd. 43.0 g. (39% recovery) II contg. about 5% I; the 50% dioxane filtrate concd. in vacuo to 170 cc., heated to boiling, and treated with an equal vol. of boiling EtOH gave 18.9% (21% recovery) I contg. only traces of II; the 50% EtOH filtrate contained about 6.5 g. (7%) mixed I and II; the 2 I fractions, combined and recrystd. twice from 50% EtOH in the usual manner, gave pure I; the VI middle fraction recrystd. from 50% dioxane and then from 50% EtOH, gave pure II; all the filtrates combined, concd. in vacuo, and treated with EtOH gave 15.2 g. (17% recovery) mixt. of 9.1 g. I and 6.1 g. II, and a 2nd crop of 5.4 g. (7% recovery) mixt. of 3.2 g. I and 2.2 g. II; the residual filtrate contained 2.4 g. (2% recovery) mixt. of 1.2 g. I and 1.2 g. II. Anhyd. I or II (1.0182 g.) suspended in 18 cc. anhyd. dioxane, treated 15 min. with a brisk stream of dry HCl, and the clear solns. dild. with equal vols. of dioxane and then with Et_2O to incipient turbidity, and refrigerated yielded 1.918 g. (88%) I.HCl and 2.030 g. (93%) II.HCl, resp.; the HCl salts were poorly sol. in fresh boiling dioxane and were recrystd. from MeOH-Et_2O to give pure samples of I.HCl, m. 160°, and of II.HCl, m. 159°. Into a suspension of 3.624 g. anhyd. I or II in 36 cc. appropriate refluxing alc. was passed a vigorous stream of dry HCl for 2.5-3 hrs., the clear soln. evapd. almost to dryness, the residual oil or paste taken up in a small vol. of the parent hot alc., and the soln. dild. with EtOH to incipient crystn. to yield the corresponding esters; the ester HCl salt which pptd. during the HCl treatment was redissolved in the hot parent alc., the soln. refrigerated overnight, filtered, and the residues washed with Et_2O and dried at 50°; small 2nd crops were obtained from the filtrates. In this manner were prepd. the following alkyl ester HCl salts of I (alkyl group, total wt. in g. of crude product, % yield, and m.p. given): Me, 4.360, 94, 160° (decompn.); Et, 4.796, 98, 140°; Pr, 4.679, 90, 131°; iso-Pr, 4.947, 95, 164°; and the following alkyl ester-HCl salts of II: Me, 4.485, 97, 180° (decompn.); Et, 4.783, 96, 178° (decompn.); Pr, 5.031, 97, 160°; and iso-Pr, 5.069, 98, 159° (decompn.). Each ester-HCl salt in Et_2O treated with NH_3 gave the corresponding free ester. In this manner were obtained the following alkyl esters (alkyl group, crystal form, % yield, and m.p. given) of I: Me, needles, 75, 62°; Et, mica plates, 77, 84°; Pr, needles, blades, 85, 59°; iso-Pr, needles, blades, 89, 75°; and of II: Me, mica plates, 89, 110°; Et, needles, 92, 86°; Pr, needles, 89, 63°; and iso-Pr, needles, 85, 75°.

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48:7161 Original Reference No. 48:1318a-i,1319a-i,1320a-i The nature of light-induced degradation products of diazo derivatives. IV. The light reaction of o-quinonediazides: photosyntheses of cyclopentadiene derivatives. Sus, Oskar; Hoffmann, Hinrich; Rosenberger, Siegfried; Kostka, Rudolf (Kalle & Co., Wiesbaden-Biebrich, Germany). Ann., 579, 133-58 (Unavailable) 1953. OTHER SOURCES: CASREACT 48:7161.

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 42, 4154i. 6-Nitro-1,2-naphthoquinone-2-diazide (2-diazo-6-nitro-1(2H)-naphthalenone) (I) in 4.5 l. AcOH and 240 cc. H2O was filtered through C and the filtrate, in sealed fermentation vessels, exposed to sunlight or ultraviolet light at 0°. The reaction was complete when an aliquot no longer coupled with phloroglucinol to form an azo dye. The soln., concd. in vacuo, gave about 8.5 g. (crude) 5-nitro-1-indenecarboxylic acid (II), pale yellow cryst. threads, m. 188-9° (from AcOH), which when heated to 185-210° gave CO2 and 5-nitroindene (III), m. 74-5° (by sublimation), also prepd. by heating II in HCO2NMe2 at 45-90°. Hydrogenation of III in EtOH by shaking with Raney Ni, steam-distg., and cooling to 0° gave 5-aminohydrindene, m. 36°; Ac deriv., m. 106° (from C6H6-gasoline). 1-Amino-2-hydroxy-7-methoxynaphthalene (10 g.) in 10% alc. HCl with 10 cc. iso-AmONO gave 9.35 g. of an HCl salt, which, when **stirred** with H2O or on attempted recrystn. from much H2O gave 7-methoxy-1,2-naphthoquinone-1-diazide, C11H8O2N2, yellow needles, m. 103-4° (from 50% alc.), which when irradiated 8 hrs. gave 5-methoxy-3-indenecarboxylic acid (IV), m. 160-1° (purified by soln. in aq. NaHCO3, pptn. with HCl, and crystn. from C6H6 or aq. MeOH); the corresponding 5-methoxyindene (V), b11 155-60°, with nerolinlike odor, was formed by heating IV in HCONMe2 under N. When the decarboxylation of IV by direct heating at about 185°, was attempted, C22H20O6, a dimer of IV, m. 235-6°, was formed. IV (0.3 g.) in AcOEt with CH2N2 in Et2O, followed by shaking successively with 2% AcOH, H2O, 5% NaHCO3 and H2O, drying the Et2O soln. with Na2SO4, and evapg. gave Me 1,3a,4,9a-tetrahydroindeno[1,2-c]pyrazole-4-carboxylate (VI). The HCl salt of 1-amino-2-hydroxyphenanthrene (VII) in 220 cc. MeOCH2CH2OH, 20 cc. 32% HCl and 40 cc. H2O, treated at 50° with 8 cc. 40% NaNO2 gave, on direct crystn. a red modification of 1,2-phenanthraquinone-1-diazide (VIIIa), C14H8ON2 m. 151° (decompn.). Diazotization of VII carried out with AmONO at 25° (or below), with subsequent cooling at about 0°, gave a yellow-green modification (VIIIb), small rods, m. 150-1° (decompn.). VIIIb could be recrystd. by rapid soln. in warm MeOCH2CH2OH contg. a few drops HCl, filtering through C and

treating the filtrate at 60° with 18% HCl to incipient cloudiness. VIII (presumably either form) in dioxane contg. 50% AcOH at 10-18°, **stirred** and irradiated with a Hg vapor lamp gave benz-6,7-indene-3-carboxylic acid, pale ochre, m. 249-50° (decompn.) (from AcOH); Me ester, colorless, m. 139°. Benz-6,7-indene m. 42° (from Et2O). A mixt. of α-C10H7CH2CO2H (15 g.), 15 g. 2,5-O2N(MeO)C6H3CHO, 45 cc. redistd. Ac2O, and dry Et3N under N, heated 12 hrs. at 100° gave 4-hydroxychrysene (IX) (not purified) (cf. Cook and Schoental, C.A. 39, 4603.5). IX (0.6 g.) in 200 cc. EtOH and 20 cc. 10% NaOH at 2° with 1.5 cc. PhN2Cl (from 1 cc. PhNH2) gave the 3-phenylazo deriv. of IX, reddish brown **hexagonal** plates, m. 248-9° (from AcOH or dioxane) which on hydrogenation with Raney Ni, soln. in hot HCONMe2 filtration through C, and treatment with EtOH gave the 3-NH2 deriv. of IX, colorless **hexagons**, not m. below 400°, 0.4 g. of which in 7.5 cc. HCONMe2 and 1.25 cc. HCl at 0-5° was treated with 2N NaNO2 giving 0.37 g. 1,2-chrysenequinone-1-diazide (X) golden yellow, darkening at 150° and charring without m., coupling very slowly with phloroglucinol in NH4OH giving a red compd. In AcOH, in direct sunlight, X gave naphth[2,1-e]indene-1-carboxylic acid, prismatic rectangles (from AcOH or EtOH) decompg. between 230 and 270° depending on the rate of heating; this on decarboxylation in HCONMe2 gave cyclopentadienophenanthrene, C17H12, colorless, m. 164-5° giving a blue color with concd. H2SO4. 4-Nitroso-5-hy droxy-2-phenyl-2Henzotriazole (11 g.) (cf. Fries and Roth, C.A. 6, 2413) in EtOH hydrogenated with Raney Ni at 70° and 60 atm. and treated with HCl, gave 5.7 g. HCl salt of the 4-NH2 analog, C12H10ON4Cl (sic), cream-colored, m. 257-60°, which in HCONMe2 with aq. NaNO2 at 0° gave XI, golden yellow, m. 200-1° (decompn.) (from dioxane), forming an azo dye with phloroglucinol which gave typical metallic lakes; XI, irradiated with a Hg vapor lamp, gave (XII), rectangles, m. 225° (decompn.) (Me ester, m. 119-20°); decarboxylation of which, either by heating directly or in HCONMe2 gave the corresponding indene, C11H9N3, needles, m. 71° (from MeOH). From 5-amino-1-methyl-1H-benzotriazole [Pinnow and Koch, Ber. 30, 2852(1897)] in hot aq. NaOH, with NaNO2, followed at 0° by the dropwise addn. of 2N H2SO4, and subnsequently by addn. of an excess concd. H2SO4 and heating 5 hrs. at 115-20° (until the mixt. no longer coupled with R acid) there was formed 13.1 g. 5-hydroxy-1-methyl-1H-benzotriazole, C7H7ON3, m. 192-3°. which with HCl and NaNO2 gave the 4-nitroso deriv., C7H6O2N4, platelets, decomp. about 227° (from AcOH); this when hydrogenated gave the 4-amino deriv. (XIII) isolated as the HCl salt (XIIIa), C7H8ON4.HCl, colorless prisms (from EtOH contg. HCl) turning yellow on drying, carbonizing gradually at about 210°, and losing HCl when heated 24 hrs. at 125° in a

drying pistol over KOH and **P2O5** giving XIII, C7H8ON4, m. 234-6° (decompn.). Treated at 0° with HCl and NaNO2, XIIIa gave (XIV), yellow needles, m. 170-1° (decompn.) (from H2O or EtOH). Irradiated in 300 cc. AcOH and 15 cc. H2O, 1 g. XIV gave 0.55 g. of compd. XV, colorless plates, m. 220-1°, not decarboxylated at 290°, and which failed to react with CH2N2, but which gave a deep red color with "Fast Blue salt BB" (XVI). Deacetylation of XV with 16% HCl gave the HCl salt of the corresponding acid, prisms, hydrolyzing readily to the free acid, C7H7O2N3 (XVII), colorless needles, m. 283-4° (decompn.), giving a play of colors in aq. NaHCO3 (turning from yellow to blue gray to blue-violet), a deep blue color with FeCl3, and a red color when coupled with XVI. XVII was also formed by irradiating XIV in H2O, in the absence of AcOH. XVII was shown to have properties totally different from those of 1-methyl-6,7-dihydroxy-1H-benzotriazole (XVIII). 2,3,4-Br(MeO)2C6H2NO2 and MeNH2 gave the 6-MeNH analog; this was catalytically reduced to 2,3,4-MeNH(MeO)2C6H2NH2 and diazotized, and treated with HBr to give XVIII.HBr, m. 210°. By coupling 1-phenyl-5-hydroxybenzimidazole (XIX) in NaOH and pyridine with p-HO3SC6H4N2Cl followed by acidification, the corresponding (unanalyzed) ochrecolored azo dye was formed, which, in NaOH with Na2S2O4, followed by acidification with AcOH, gave the 4-NH2 deriv. of XIX, colorless prisms, m. 211-12° (decompn.), yielding, on diazotization (XX), yellow, m. 162-3° (from 90% EtOH). Irradiated 2 hrs. in AcOH and H2O, XX gave C15H12O3N2 (XXa), m. 202-6°, contg. an Ac group, and apparently analogous to XV, and, like the latter, could not be decarboxylated by heating in N. 2,4-H2N(O2N)C6H3NHPh (79.6 g.) triturated with 38 g. BzH, heated 15 min. with PhNO2 cooled, and treated with 50 cc. EtOH and HCl gas, gave 58 g. 5-nitro-1,2-diphenylbenzimidazole m. 180-1° (from AcOH) readily reduced to the 5-NH2 analog, m. 191-2°, which, when diazotized in aq. H2SO4 at 0°, followed by heating (until there was no further coupling with R acid), dild. with H2O, and neutralized with NaOH gave the 5-hydroxy analog, C19H14ON2 (XXI), m. 249-50° (decompn.). With p-HO3SC6H4N2Cl, XXI gave the azo dye, C25H18O4N4S (XXII), ochre-colored, charring when heated. XXII in aq. NaOH with Na2S2O4 gave the 4-amino deriv., C19H15ON3 (XXIII), of XXI, m. 206-9°, isolated as the yellow Na salt (XXIIIa), the HCl salt, or as the AcOH salt [C21H19O3N3, pale yellow prisms, m. 211-12°, losing AcOH when kept in vacuo over KOH (giving XXIII)]. XXIIIa (prepd. from 13.5 g. XXII) in 50 cc. 16% HCl, filtered through C, cooled to 0° and treated dropwise with NaNO2 gave the 2-Ph deriv. of XX, orange needles, m. 157-8° (decompn.), which when irradiated in aq. AcOH gave the 2-Ph deriv. (XXIV) of XXa, colorless rhombs, m. 222-3°. 1,2-Naphthoquinone-2-diazide-5-sulfonyl chloride (XXV) (Ger. 865,410) and PhNH2 in C6H6 gave the corresponding

5-sulfanilide (XXVI), $C_{16}H_{11}O_3N_3S$, yellow needles, m. 168-9° (from C_6H_6 or EtOH), which when irradiated in dioxane contg. HCl gave 4-phenylsulfamoyl-1-indenecarboxylic acid, colorless, m. 183-4° (decompn.) (from Me_2CO-H_2O), Me ester, m. 188-9°. Prepd. similarly to XXVI was 4-sulfamoyl-1,2-naphthoquinone-2-diazide golden yellow, m. 162°, giving, on irradiation, 3-phenylsulfamoyl-1-indenecarboxylic acid, pale yellow, m. 151-3° (from AcOEt by the addn. of petr. ether). To 1.6 g. XXVI in 20 cc. dioxane, 3.1 cc. 2N NaOH, and 8 cc. H_2O (at or below 20°) was added 1.6 g. XXV in 10 cc. dioxane, giving N,N-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthylsulfonyl)aniline (XXVII), alkali-insol., m. 145.5-6.0° (decompn.) (from AcOH). Irradiated at 0° in sunlight, XXVII gave the expected deriv., $C_{26}H_{19}O_8NS_2$, m. 249-50° (decompn. from AcOH). From Na 6-hydroxy-1,2,3,4-tetrahydro-7-naphthalenesulfonate and p-$MeC_6H_4SO_2Cl$ was formed the 6-tosylate [isolated as the Na salt, m. 128-9° (decompn.)], converted by PCl_5 into the sulfonyl chloride, $C_{17}H_{17}O_5S_2Cl$, **hexagons**, m. 133-4°, from which was prepd. the 7-sulfanilide, prisms, m. 157-8°; this on sapon. with NaOH in alc. gave 6-hydroxy-1,2,3,4-tetrahydro-7-naphthalenesulfanilide (XXVIII), thin rhombs, m. 183-5° [Na salt (XXVIIIa), nacreous **hexagons**]. To 38 g. XXVIIIa in 400 cc. 2.5% NaOH, 400 cc. dioxane and 5 cc. pyridine at 0° was added very gradually PhN_2Cl (from 17 g. $PhNH_2$.HCl), acidified with 30% HCl, and crystd. from dioxane contg. 5% AcOH giving 19 g. 8-PhN_2 deriv. of XXVIII, m. 237-8° (decompn.), which when reduced with Hoechst Ni catalyst in alc. at 60 atm. and 80°, dissolved in 8% NaOH, washed with Et_2O, filtered through C, and acidified with AcOH gave 9 g. of the 8-NH_2 deriv. of XXVIII, m. 160° (never completely purified because of its ready oxidation), which, by the usual method was converted into the diazide (XXIX) orange-yellow, m. 160-5° (decompn.), giving, when irradiated 1.5 hrs. in sunlight, XXX, $C_{16}H_{15}NO_3S$, tan amorphous powder. To 12 g. 1,2,3-$H_2N(HO)C_{10}H_5CONHPh$ in 540 cc. EtOH was added 4.2 g. $Cu(OAc)_2$ in 108 cc. glacial AcOH and 42 cc. 2N $NaNO_2$; the mixt. warmed to 50-60° gave the expected oxo-diazo compd., yellow, m. 167-8° (from AcOH) giving after an 11 hrs. irradiation the indene deriv., $C_{17}H_{13}O_3N$, m. 141° (decompn.) (best purified by soln. in aq. $NaHCO_3$ and pptn. with HCl); 2-indenecarboxanilide, $C_{16}H_{13}ON$, irregular **hexagons**, m. 180-1°.

CC 10 (Organic Chemistry)

L57 ANSWER 19 OF 20 HCA COPYRIGHT 2004 ACS on STN

42:36467 Original Reference No. 42:7724e-i,7725a The N-substituted derivatives of p-toluenesulfonamide. Cerkovnikov, E.; Tomasic, P. (Institute Hygiene, Zagreb). Arhiv Kem., 19, 38-41;in English, 41-42 (Unavailable) 1947.

GI For diagram(s), see printed CA Issue.

AB The starting material in each case was p-MeC6H4SO2Cl (I) which was treated with the corresponding amine in acetone at comparatively low temps. The product was always dried under a high vacuum over **P2O5** at 80° about 2 h. for anal. To 19 g. I and 12.2 g. guanidine nitrate in 60 cc. acetone at 0° was added 40 g. 20% NaOH soln. at such a rate that the temp. did not rise above 15°, the mixt. **stirred** 2 h. at room temp., and the product pptd., filtered with suction, and recrystd. from EtOH, giving 8.8 g. (38.1%) N-guanyl-p-toluenesulfonamide, C8H11N2O2S.H2O, m. 207-8°, crystd. like sulfaguanidine with 1 mol. water. The same method as above, using 60 cc. solvent, 19 g. I, 9.4 g. 2-aminopyridine, and 20 g. NaOH soln., gave 9.0 g. (36.3%) N-2-pyridyl-p-toluenesulfonamide, C12H12O2N2S, needles from MeOH, m. 213-14°. From 19 g. I and 9.5 g. 2-amino-4-methylpyrimidine in 60 cc. acetone in the presence of 20 g. 20% NaOH, 9.0 g. (34.2%) N-(4-methyl-2-pyrimidyl)-p-toluenesulfonamide, C12H13O2N3S, **hexagonal** prisms from H2O, m. 226.5-8°, was obtained. The condensation product, C17H16N2O4S3 (II), of I and 2-aminothiazole (1.2 g. from 5.7 g. I and 3.0 g. 2-aminothiazole in 18 cc. acetone and 6 g. 20% NaOH) m. 150-1° (from EtOH). The 2-aminothiazole used reacted in its tautomeric form and all attempts to prep. N-2-thiazolyl-p-toluenesulfonamide failed. N - 8 - Quinolyl - p - toluenesulfonamide, C16H14O2N2S (20.2 g. crude product (67.8%) from 19.0 g. I and 14.4 g. 8-aminoquinoline in 60 cc. acetone with 20 g. 20% NaOH), tetrahedrons from acetone, m. 153°. N-(6-Methoxy-8-quinolyl)-p-toluenesulfonamide, C17H16O3N2S (4 g. crude product (61%) from 3.8 g. I and 3.5 g. 8-amino-6-methoxyquinoline in 12 cc. acetone with 4 g. 20% NaOH) in. 131-2° (from acetone). All above compds. were tested in vitro against the different strains of the dysentery bacillus (Schiga, Schmitz, Flexner II and III, Boyd I and V). They were also tested against streptococcus and pneumococcus (types not stated). The method of culturing in solid media was used in each case. None of these compds. in a 2% soln. was found bacteriostatic against any one of the listed pathogenic organisms. 8 refs..

CC 10 (Organic Chemistry)

L57 ANSWER 20 OF 20 HCA COPYRIGHT 2004 ACS on STN

14:15544 Original Reference No. 14:2893h-i,2894a-i,2895a-i,2896a
Contribution to the chemistry of phosphomolybdic acids, phosphotungstic acids and allied substances. Wu, Hsein Journal of Biological Chemistry, 43, 189-220 (Unavailable) 1920. CODEN: JBCHA3. ISSN: 0021-9258.

AB Allowing M to represent Mo or W, the complex H3PO4 compds. of these elements fall into 2 groups: 1. Acids containing 1 mol. **P2O5** to 18 or to 24 mols. MO3, known in this abstract as 18-or 24-acids, resp., which are colored except for the 24-W compd., are sensitive

to reduction and are pptd. by pyridine in dil. soln. In alk. soln. they are converted into substances of group 2. These are salts with a number of different **P2O5**:MO3 ratios, all are colorless, do not ppt. pyridine in dil. soln., are not sensitive to reduction and are converted by mineral acids of group 1. The formation of the complex acids depends upon the concn. of the reacting substances, the temp. and the acidity. The concns. affect the result according to the laws of mass action; the 24-acids may be formed at room temp. but 18-acids require boiling. The most important factor is the acidity. H3PO4 and Na2MoO4, mixed in any proportion, will not form a complex acid. The addition of HCl equiv. to the Na2MoO4 is followed by the formation of a mixt. of the 18- and 24-acids. The yield of the latter increases with the acidity. In a mixt. of 1 mol. Na2WO4 and 4 mols. H3PO4, all the W is converted into the 18-acid. If HCl be added, the 24-acid is formed almost exclusively. The Mo acids are readily interconvertible; the W acids are more stable. Phospho-24-molybdic acid. Dissolve 100 g. Na2MoO4.2H2O in 200 cc. H2O, add 10 cc. 85% H3PO4, 100 cc. concd. HCl and 150 cc. Et2O and shake in a 1. sepg. funnel. Cool. After 10-5 min. transfer the lowest of the 3 layers to another funnel. Add 100 CC. H2O, shake; add 50 cc. concd. HCl and some more Et2O and shake again. Cool and again remove lowest layer and repeat the washing. Transfer to a beaker, add 25 cc. H2O and a few drops concd. HNO3 and evap. on the H2O-bath until crystals form on the surface. Allow to cool slowly. Yellow octahedra, 3H2O.**P2O5**.24MoO3 + 59H2O. Phospho-18-molybdic acid. Dissolve 100 g. Na2MoO4.2H2O in 450 cc. H2O, add 15 cc. 85% H3PO4 and 80 cc. concd. HCl and boil for 8 hrs. with reflux. Cool. **Stir** in 100 g. powdered NH4Cl. Filter as dry as possible on a Buchner filter. Dissolve in an equal wt. of H2O and filter off the NH4 salt of the 24-acid on hardened paper. Add 20% NH4Cl without stirring, let stand 4-8 hrs., filter dry as possible on a Buchner filter, dissolve in a little H2O and evap. in vacuo at not over 40° until crystals begin to form. Cool slowly to 5-6°. Filter dry as possible. Disconnect the suction, cover the crystals with dry Et2O, **Stir**, let stand a few min., and suck dry. Dry quickly. Orange crystals, 3(NH4)2O. **P2O5**.18MoO3.11H2O. The free acid is liberated with concd. HCl, is extd. with Et2O washed and evapd. as in case of the 24-acid, but at low temp. (20°). Orange prisms, 3H2O.P2O518MoO3.11H2O. Phospho-24-tungstic acid. Dissolve 100 g. Na2WO4.2H2O in 100 cc. warm H2O, add 10 cc. 85% H3PO4 and 80 cc. concd. HCl Allow to cool and after at least 4 hrs. filter as dry as possible, redissolve in 120 cc. H2O add 70 cc. Et2O and 40 cc. concd. HCl and extract, wash and evap. as in case of the 24-Mo acid. Colorless octahedra, 3H2O.**P2O5**.24WO3.59H2O. This is the chief ingredient of the comm. phosphotungstic acid, which is not pure, the Merck and Kahl-baum. prepns. containing 10% of the 18-acid. Phospho-18-tungstic acid exists in 2 forms, A and B.

Dissolve 200 g. Na2WO4.2H2O in 1000 cc. H2O. Add 280 g. 85% H3PO4 and boil for 8 hrs. under a reflux, allowing the soln. to evap. to 1000 cc. toward the end of this period. Add a few drops Br-H2O, cool and add 200 g. powdered NH4Cl **Stir** and filter on a Buchner filter. Dissolve in H2O and reppt. with NH4Cl. Repeat. Dissolve in 600 cc. H2O at 50° and keep at 37°.
Crystals of NH4 A-phospho-18-tung-state sep. in a few days. When no more form, decant the liquid, wash the crystals with ice-cold H2O and recryst. 5 times from H2O. Yield 30 g. of tough, lemon-yellow crystals, 3(NH4)2O.**P2O5**.18WO3.16H2O, **hexagonal**
prisms terminated by 1 or 2 rhom-bohedra, which do not readily lose H2O of crystn., soly. 51 g. in 100 g. H2O; the B form, 3(NH4)O.P2O5WO3.18H2O, crystallizes on longer standing; it consists of thin, brittle, pale yellow, rhomboidal plates with truncated edges, which easily lose H2O. Soly. 122 g. in 100 g. H2O. The A form yields 30% more blue color when treated with uric acid and Na2CO3: than does B. The color developed by the former has a tint of green, that by B, violet. The acids are set free by HCl, extd. with Et2O and evapd. on the H2O bath. A-Phospho-18-tungstic acid, **P2O5**.18WO3.38H2O. B-Phospho-18-tungstic acid, **P2O5** .18WO3.40H2O. The methods for analysis of the complex phosphotungstic and -molybdic acids were: **P2O5**; Dissolve 2.5-3 g. material in 25 cc. warm H2O, add 25-30 cc. 10% NaOH, heat to boiling until the ppt. has redissolved and then at slightly lower temp. for 20 min. longer. Cool and add 5-6 g. NH4Cl, 10-15 cc. magnesia mixt. (55 g. MgCl2.6H2O, 140 g. NH4Cl and 350 cc. concd. NH4OH per liter) and 0.25 vol. concd. NH4OH. After 4 hrs. filter and wash with 1:4 NH4OH. Ignite the ppt., digest the ash with 15 cc. 2N HCl for 1 hr. at 80-90°, filter on a small paper and wash with ten-cc. portions of 0.5 N HCl. Add 5 cc. magnesia mixt. and, very slowly, 25 cc. concd. NH4OH. Filter after 4 hrs., wash with 1:4 NH4OH, ignite and weigh. Correct for blank. If no W, but only Mo, is present, the heating with NaOH and the double pptn. may be omitted, for the complex acid is decompd. by NH4OH at ordinary temp. WO3: On ignition, P is always lost, so that the correct WO3 content is detd. by weighing the ignited residue, detg. the **P2O5** content therein as above and subtracting. NH3 is detd. by distn. and H2O by difference. A number of the mixed complex acids, containing both Mo and W, were also prepd. by essentially the same methods. In general, their properties resemble those of the corresponding acid containing only the predominant element. The sensitivity to reduction with Na2SO3, is roughly parallel to the Mo content. The color changes from bluish green to violet as the proportion of W is increased. The 24-acids were not investigated in detail. The "phenol reagent" of Folin and Denis (cf. C. A. 6, 2245; 13, 2541, 2545) is one of the mixed 18-acids and these were studied more carefully. In the absence of a strong acid, the acid formed contains much W and is not sensitive to reduction, no matter how

much MoO_3 is used. The greater the amt. of MoO_3 to be incorporated, the greater is the concn. of HCl required. If too much HCl is used, some 24-acid may be formed. The acid of the "phenol reagent" is prepd. as follows: Dissolve 100 g. $Na_2WO_4.2H_2O$ and 25 g. $Na_2MoO_4.2H_2O$ in 700 cc. H_2O. Add 50 cc. 85% H_3PO_4 and 100 cc. concd. HCl. Boil under a reflux for 8 hrs. (Dil. for use as reagent.) Sat. the cooled soln. with NH_4Cl, filter, redissolve in warm HO and filter off the yellow insol. residue. If the NH_4 salt is desired, salt out again and recryst. from warm H_2O. It consists of a mixt. of $3(NH_4)_2O$.**P_2O_5**.$13WO_3.5MoO_3.10H_2O$ and $3(NH_4)_2O$.**P_2O_5**.-$14WO_34MoO_3.10H_2O$. The free acids are obtained in Et_2O soln. as usual and the soln. is evapd. at low temp. A number of NH_4 salts of the reduced phosphomolybdic acids were also prepd., the extent of the reduction being detd. by titration with $KMnO_4$. The method of reduction is indicated. $3(NH_4)_2O$.**P_2O_5** .$17MoO_3.MoO_2.H_2O$, excess of Fe'' in acid soln., 20% NH_4Cl, black crystals. $3(NH_4)_2O$.**P_2O_5**.$16MoO_3.2MoO_2.H_2O$, from 10 g. NH_4 salt of 18-acid, 50 cc. H_2O, 5 cc. 40% HI and 5 g. $NaHSO_3$, standing 24 hrs., 10 g. NH_4Cl, black crystals. $3(NH_4)_2O$.**P_2O_5** .$16MoO_3.Mo_2O_5.H_2O$, from 10 g. NH_4 salt of 18-acid, 50 cc. H_2O, 5 cc. 40% HI, satn. with H_2S, standing 24 hrs., 10 g. NH_4Cl, black crystals, violet reflex. $3(NH_4)_2O$.**P_2O_5**.$22MoO_3.2MoO_2.H_2O$, 10 g. of the 24-acid, 50 cc. H_2O, 5 cc. 40% HI and 5 g. $NaHSO_3$, 10g. NH_4Cl at once, blue powder. $3(NH_4)_2O$.**P_2O_5** .2oMoO3.$4MoO_2.H_2O$, as preceding, but standing 24 hrs. before adding NH_4Cl, black ppt. A number of interesting applications of these complex acids in analytical chemistry are indicated. Detection of Cu: Add a few drops 5% KCN, acidify with HCl, add a few drops "phenol reagent." If more than a trace of Cu is present the mixt. will become blue at once; otherwise it is yellow but becomes blue on addition of Na_2CO_3; sensitivity, 1:5,000,000. Detection of **P_2O_5**: Add 1-2 CC. 2% $(NH_4)_2MoO_4$ soln., 2-3 CC. 10% KI, 1 cc. 10% $NaHSO_3$ and 1-2 cc. concd. HCl, After 10-20 min. make alk. with Na_2CO_3; blue color indicates **P_2O_5**. Sensitivity, 1:1,000,000 of P. Deln. of **P_2O_5**: To the unknown soln. containing 0.1 to 0.2 mg. P in 5 cc. in a 50-cc. flask, add 5 cc. each of 10% $NaHSO_3$, 10% KI, 2% $(NH_4)_2MoO_4$ and 1: 1 HCl. Similarly treat 5 cc. of standard soln. containing 0.15 mg. P. Cover the, flasks and allow to stand 2 hrs. Add to each 10 cc. 20% Na_2CO_3, shake to hasten the escape of CO_2, dil. to 50 cc. and compare in a colorimeter. The color developed is not max., but is proportional to the amt. of P within the range 0.1-0.22 mg. Application to oxidation-reduction reactions in presence of F'' is also indicated.

CC 6 (Inorganic Chemistry)